A TREATISE
ON
PHYSICAL CHEMISTRY

VOLUME ONE

A TREATISE
ON
PHYSICAL CHEMISTRY

A Co-operative Effort by a Group of Physical Chemists

EDITED BY
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In Two Volumes, Illustrated

VOLUME ONE

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"It is also true that man sees more of the things themselves when he sees more of their origin; for their origin is a part of them and indeed the most important part of them. Thus they become more extraordinary by being explained. He has more wonder at them but less fear of them; for a thing is really wonderful when it is significant and not when it is insignificant."

G. K. CHESTERTON—"St. Francis of Assisi."

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PREFACE

An adequate treatment of the subject of modern physical chemistry for the advanced student is a difficult task for any one person. The ever-widening scope of the subject, its extension into domains which, even a decade ago, were as yet unknown or unexplored, demand qualities of broad scholarship on the part of an author which are largely incompatible with the call for specialized endeavor in other phases of his work. The present treatise on physical chemistry represents, therefore, a coöperative effort on the part of a number of physical chemists to cover generally the major portions of their science by contributions in those portions of the subject which their particular inclinations have led them more especially to study and to which they themselves may have contributed by their own effort and research. It is hoped that, in this way, a more authoritative treatment of the several branches of the subject may have been achieved; perhaps, also, a fresher exposition of the subject in its various phases may have been realized. Through coöperation, it should have been possible to secure a more up-to-date record of the present status of the science, since the time consumed in the preparation of such a treatise can obviously be reduced beyond the limits which must be demanded by a single author. Furthermore, where labor is shared a more frequent revision can be more easily achieved.

Coöperation in the present undertaking has been freely and generously given. The editor wishes to express, therefore, his gratitude for such assistance. The responsibility for the plan of the book must rest with him, since his contributors have, in the main, acceded to his requests as to the general trend of their contributions. It will be generally recognized that a new era in physical chemistry is upon us. The science of a decade ago is utterly inadequate to present-day demands. The atom is no longer a philosophical concept but a concrete reality, no longer however "atomic" or indivisible. Energy is considered less and less as a continuum, more and more in units or quanta. The contributions of thermodynamics, of statistical averages, are, more and more, being supplemented by studies of the individual. The classical tradition of physical chemistry was the study of the individual from the behavior of the crowd. Are there not signs that the behavior of the crowd can be deduced from the study of the individual? It is with such thoughts in mind that the plan of the book took shape. Atomistics and kinetics must supplement the general conclusions of statistical and thermodynamic research. The modern student must avail himself alike of all the varied avenues of approach to the unexplored terrain.

The book is addressed primarily to the advanced student in physical chemistry, to the research student desirous of learning the background to his problem and to the research man in industry who requires the theoretical treatment of his practical investigations. Actually, however, the book may have a wider appeal. As divided into two volumes, the work appears to meet the demand for a graduated text in physical chemistry. The material of the first volume represents that portion of the subject of theoretical chemistry that can with advantage be addressed to the first year student of physical chemistry who plans to continue his studies beyond that year. It contains the main features of the classical era of physico-chemical development. The volume contains, it is true, a more detailed treatment of the subject than the average student will fully grasp in his first year of its study. It will not, however, be amiss for the serious student to find in his text somewhat more than will be discussed in his lectures and exercises. Stimulation to further effort may result. For all students who plan to take more than one year of work in physical chemistry, assimilation of the material of the first volume will represent a very solid accomplishment and a sound basis for approach to the more modern aspects of the subject which find their treatment in the second volume. In the latter, the student is taken to the borderland of the subject where active development is even now in progress.

A coöperative text offers a fruitful field for the critic or reviewer anxious to locate the weaknesses of a text rather than its virtues. To such people it will be well to point out that an editorial survey has resulted in the discovery of many places in the book where duplication occurs and even where apparently divergent views have found expression. Many of these have been carefully considered and discussed with collaborators and colleagues and have been allowed to remain. For, where divergent views are held, there is evidently something lacking in absolute truth of the matter discussed. Such passages may therefore be taken by the student as the signposts to further research and investigation. It is with the hope that these volumes may lead to a fuller investigation of the fundamental theoretical bases upon which all the fine structure of the modern science of chemistry, academic and applied, has of necessity to stand that the labor involved in their preparation has been unremittingly given. Other tasks and endeavors would, doubtless, in many cases have been preferred. The editor gratefully acknowledges the whole-hearted coöperation of his contributors and the efforts which they have made to facilitate his work, not only in their own contributions but also in their discussion of the efforts of others. In particular, an expression of gratitude is here made to Dr. T. J. Webb, of Princeton University, who possessed, in large measure, qualities of editorship which the editor himself lacks and who has perused, and criticized, with many valuable suggestions, all of the material included in these volumes. To my brother, Dr. H. Austin Taylor, who has shared generously in the labors of index and proof my thanks are also due. The efforts which the publishers have put forth are revealed in the quality of the printing and the make-up of the book. But, beyond this obvious coöperation, there is a wealth of effort in which their anxiety to surmount difficulties with generosity has been most conspicuous. For this they deserve especial thanks.

HUGH S. TAYLOR.

PRINCETON, N. J.,
July, 1924.

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CHAPTER 1

THE ATOMIC CONCEPT OF MATTER

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The inception of the modern era in chemical science may be attributed to the proposal of the atomic theory of chemical action by John Dalton in the first volume of his New System of Chemical Philosophy, 1808. The scientific era in which the Daltonian concept was formulated was especially favorable to its development. The theory of atomic constitution was no new theory. The Greek theory of atoms, due to Leucippus and handed down to us in the writings of Democritus, is the first of which we have record. Boyle included in his conception of elementary substances some notions of atomic constituents. Dalton himself was led to the atomic theory by reason of his admiration of the Newtonian doctrine of the atomic constitution of matter. The quantitative era into which Dalton's theory was born provided the circumstances necessary and favorable to its growth. The theory simplified and correlated much that the quantitative spirit had disclosed and had not yet explained. It provided the framework upon which was built the chemical philosophy and the chemical research of the nineteenth century. Towards the close of the century it seemed as though the theory might give way to an interpretation of the science based upon energetics. But, in the new century it emerged once more broadened and amplified by the discoveries of sub-atomic phenomena.

The atomic theory of Dalton postulated the existence of minute indivisible particles or atoms, each of equal weight for the same element, atoms of different elements, however, having different weights. Compounds were the result of union of dissimilar atoms the ratio of whose weights was proportional to their combining weights This fundamental idea of atoms having characteristic weights and combining to form chemical compounds at once illuminated the quantitative facts of chemical combination then known. They may be thus briefly summarized:

(1) *The Law of Definite Proportions*, established experimentally by Proust in 1799. The elements which form a chemical compound are united in it in an invariable ratio by weight, which is characteristic of that compound. Proust's analyses were made with carbonate of copper, artificial and natural, the two oxides of tin and the two sulphides of iron. Proust showed, in contradiction of claims put forward by Berthollet on behalf of variable composition due to mass action, that when a metal combines with oxygen in more than one proportion there is no gradual increment of one element but a sudden, *per saltum*, increment. His analytical work was not sufficiently accurate to establish the law of multiple proportions.

(2) *The Law of Multiple Proportions*, deduced from experimental work by Dalton and formulated by him in conformity with his preconceived atomic theory. When an element

combines with another to form more than one compound the masses of the second element combining with a fixed mass of the first element bear a simple ratio to one another. The accurate analyses of Berzelius provided abundant evidence of the truth of this law which the less accurate efforts of Dalton produced.

(3) *The Law of Reciprocal Proportions*, established by the experimental work of Richter (1792–1794). When two or more elements combine with a third in certain proportions they combine with each other in the same proportions or in multiples of these proportions. In his book *Stoichiometry of the Chemical Elements* published in the above years this law of reciprocal proportions is illustrated.

The Law of Conservation of Mass., formulated by Lavoisier in 1774 upon the basis of experimental measurement, states that the total mass of the reactants in a chemical reaction is equal to the total mass of the products of reaction. All these laws, quantitatively exact and experimentally verifiable, fitted admirably into the framework of chemical principles established by Dalton's Atomic Theory. Further support was quickly forthcoming. Gay Lussac put forward in 1808 his *Law of Combining Volumes*. When gases combine they do so in simple ratios by volumes, the volume of the gaseous product bearing a simple ratio to the volumes of the reactants when measured under the same conditions of temperature and pressure. An attempt by Berzelius to interpret this law in terms of the atomic theory failed owing to a lack of understanding of the differences between atoms and molecules. Knowing, as a result of the earlier investigations of Gay Lussac, that many gases vary similarly when subjected to temperature, and, from the investigations of Boyle, to pressure changes, Berzelius suggested that equal volumes of different gases under like conditions of temperature and pressure contain the same number of atoms.

Avogadro's Hypothesis: The correct correlation of the atomic theory with the characteristics of ideal gases is due to Avogadro who propounded in 1811 the Avogadro hypothesis. Though not accepted by the early proponents of the atomic theory and only commanding general adherence after the exposition of the hypothesis some 47 years later by his fellow countryman the Italian scientist Cannizzaro, the hypothesis of Avogadro was a true exposition of the facts concerning gases. The hypothesis may be stated in the following terms: Equal volumes of different gases under the same conditions of temperature and pressure contain the same number of molecules. The limitations of this hypothesis as regards actual gases and the many experimental methods which have now been developed actually to determine the number of molecules in a given volume of gas will be dealt with in appropriate portions of the following chapters. At this stage it will suffice to indicate the actual change introduced by the Avogadro hypothesis into the Daltonian concept of atoms and atomic combinations. On the Avogadro principle the atom became the smallest particle which can enter into chemical combination. The molecule became the smallest particle of matter which was capable of independent existence. This distinction clarified the known experimental facts. It explained for example how one molecule of hydrogen and one molecule of chlorine combined to form two molecules of hydrogen chloride. Each molecule of hydrogen and chlorine contained two atoms whereas the molecules of hydrogen chloride contained an atom each of hydrogen and chlorine. It is perhaps advisable to point out, now that the difficulties associated with the terms atom and molecule no longer exist, that the definition of the molecule given above lacks somewhat in rigor. For, we now know that, under proper conditions, not only molecules of diatomic gases such as hydrogen, chlorine and iodine may exist in the free state but that atoms may also so exist provided the conditions of temperature and pressure be suitably chosen. Under such conditions the molecule and the atom become identical.

With the atomic theory as guide, Berzelius proceeded to the determination of atomic weights of a wide variety of elementary substances. The determination involves two steps, (1) the measurement of the combining weight and (2) the finding of the ratio of combining weight to atomic weight. The former is an experimental operation generally involving some kind of quantitative analytical procedure as, for example, the determination of the quantities of potassium and chlorine in unit quantity of potassium chloride, of hydrogen and oxygen in water or of hydrogen and chlorine in hydrogen chloride. From such determinations the combining weights of oxygen, chlorine and potassium in terms of hydrogen as unity may be determined. The second step, however, involves a knowledge of the number of atoms which are combined in a compound with the reference element. Thus, to take an example of historic interest, the atomic weight of oxygen relative to that of hydrogen as unity would be approximately 8 or 16 according as one or two hydrogen atoms combine with one atom of oxygen, the combining weight being 8. It is in the solution of this problem that the Avogadro hypothesis performed a most useful function, delayed, however, by the non-recognition of the importance of the hypothesis until Cannizzaro's demonstration of its utility in such connection. Until that demonstration was given, no general agreement as to atomic weights was possible, different observers using different values which, however, were simple multiples of other values for the same element, according to the preconceived idea of the experimenter as to the atomic ratios prevailing in the compound analyzed.

Dulong and Petit's Law: Two further principles of great utility in deciding doubtful cases of atomic weight values were discovered and employed in the early years of the atomic theory. The one, the law of Dulong and Petit was applicable to solid elementary substances. The law, formulated in 1819, states that the product of the atomic weight and the specific heat is approximately 6 calories. It will be shown that this law is a limiting law applicable to all solid elements under specified conditions. Known exceptions, such as boron and carbon, which show low atomic heats at ordinary temperatures manifest at those temperatures a phenomenon common to all solid elements if the temperature chosen for the determination be sufficiently low. At higher temperatures, even these elements have atomic heats approximating those demanded by the law. Nevertheless, a sufficiently large number of elements obey the Dulong and Petit relation at ordinary temperatures as to make this principle of important assistance in deciding cases of doubt in reference to atomic weights deduced by other methods.

Isomorphism: The second principle was of assistance in the study of the atomic weights of elements present in crystalline compounds. In 1820 Mitscherlich called attention to the practical identity of crystalline forms of the corresponding salts of phosphoric and arsenic acids. They crystallized with the same molecular quantities of water of crystallization and possessed the power of forming mixed crystals. As a result of such observations, Mitscherlich concluded that analogous elements or groups of elements can replace one another in compounds without material alteration of crystalline form. Two compounds so related were termed isomorphous and the phenomenon was given the name Isomorphism. The identity of form is not absolute. The distances between atoms varies slightly in one compound from that in the compound of the next analogue. These differences persist even in the mixed crystal and result in distortion of the crystal angles. The variation of interatomic distances and the distortion of the crystal angles become greater the more widely divergent are the analogous elements. As a consequence, with the more widely divergent analogues, mixed crystals will not occur even though there is identity of crystal form between the compounds. Substances may crystallize in two or more distinct crystallographic systems having, nevertheless, constant chemical composition. Such behavior is termed dimorphism. If isomorphism occur between the two forms severally of two such dimorphous bodies the bodies are said to be isodimorphous, the phenomenon being, correspondingly, isodimorphism. Similarly, trimorphous substances are known.

From the standpoint of the atomic theory, however, quite apart from the importance of Mitscherlich's observations crystallographically, isomorphism assisted greatly, since it gave a ready indication of chemical composition in the case of substances crystallizing in the same form and isomorphously with substances of known composition. Berzelius made great use of the principle in fixing atomic weights and in checking the results of his analytical investigations. Isomorphism has acquired a still greater range of applicability as the result of more recent deductions concerning the sub-atomic characteristics of the atom. As will be later demonstrated, isomorphism is possible between compounds containing elements which from the Mitscherlich standpoint would not be regarded as analogues but which, from a similarity of sub-atomic components, acquire identity of crystalline form. (See Chapters V and XVI.)

Prout's Hypothesis: Philosophically considered, the Daltonian concept of atoms, of differing weights but incapable of subdivision, is not without difficulties. Reason suggests the possibility of subdivision even though technique may not be adequate to its achievement. As a consequence, side by side with the many achievements of theoretical chemistry in the 19th century, based fundamentally upon the atomic theory, there has persisted the essentially opposite viewpoint, namely that of continuity or unity of matter as opposed to the discontinuous view of material substances which the atomic theory postulates. This contrary viewpoint has been developed both consciously and unconsciously. Prout's hypothesis put forward in 1815 is the earliest illustration of conscious development. Prout, reasoning from the approximation to whole numbers of the atomic weights of several of the elements, suggested that the elements might be, in reality, polymers of hydrogen. This was a revival of the protyle theory of matter with quantitative investigations as its support. But further quantitative study tended to withdraw support from the hypothesis of Prout. The hypothesis gave an added stimulus to exact atomic weight determinations and these but served to demonstrate effectively that many of the atomic weights were markedly divergent from whole numbers. Stas' determinations of atomic weights, and notably that of chlorine, were classical researches, with this divergence from the whole number rule as the decisive result.

Döbereiner's Triads: Attempts at classification of the elements on the basis of similarity of properties are less conscious methods of establishing the essential unity of matter. Thus, Dobereiner's observation, in 1817, that groups of three elements chemically similar, with atomic weights in arithmetic progression, could be compiled, while essentially an attempt at convenient classification, involves, in its fundamentals, an appreciation of a unifying principle. The chemical similarity of, for example, lithium, sodium and potassium, chlorine, bromine and iodine, calcium, strontium and barium, sulphur, selenium and tellurium with the very definite arithmetical relationships of their atomic weights, Na − Li = 16.06, K − Na = 16.1, suggests immediately a fundamental factor common to each group of three and so some unity underlying each group. This aspect of the matter was not, however, emphasized either in Döbereiner's triad system nor in subsequent, more comprehensive, systems of classification.

Faraday's Laws of Electrolysis and the Electrochemical viewpoint. The electrochemical researches of Nicholson and Carlisle, 1800, on the decomposition of water, of Davy on the preparation of potassium, sodium, and other metals 1807–1808, and of Berzelius and Hisinger in Sweden 1803–1807, on the decomposition of neutral salts by the electric current, definitely brought electrochemistry to the fore as an auxiliary to other methods of chemical investigation. Davy's Electrochemical theory of affinity and Berzelius' theory of atomic polarization brought electrochemistry into the domain of theoretical chemistry. Faraday's researches in experimental electricity established quantitatively the relationship between electricity and the atomic weights of the elements. Faraday observed that (Experimental Researches, 505): 'For a constant quantity of electricity, whatever the decomposing conductor may be, whether water, saline solutions, acids, fused bodies or the like, the amount of electrochemical action is also a constant quantity.' Furthermore, with different solutions, the amounts of elementary constituents produced by unit quantity of electricity are proportional to their chemical equivalents. In these two laws the atoms and electricity are for the first time intimately associated. Faraday's ions, transferred through solutions by the agency of the current, were carried in definite amounts, one gram ion for every 96,500 coulombs of electricity. Modified by Grove, 1845, by Williamson in 1851, and by Clausius, 1857, in the sense that the decomposition was not effected by the current but that the ion carriers must exist in part uncombined, the theory of conduction was given quantitative formulation by Arrhenius, 1887, who demonstrated that the extent to which the free ions occurred in solution was deducible from the electrical conductance of the solution as well as from the properties of solutions, at that time entirely disassociated from the electrical properties of solutions, namely, osmotic phenomena, freezing point, boiling point and vapor pressures of solutions. The properties of conducting solutions became a function of the positively and negatively charged ions which they contained. Progress from this point of view to those held today came as a result of the researches of the physicist and the student of radioactive change.

The Periodic System of Classification: Before the contributions of the physics of the atom and of radioactivity were achieved, the chemist had provided himself with a broad and comprehensive system of classification of the elements which, more decisively than hitherto, suggested a fundamental unity of elementary structure, though designed, primarily, to emphasize the interrelation of chemical and physical properties. An effort of de Chancourtois (Vis Tellurique, Classement naturel des Corps Simples, 1862) excited little attention among chemists, though substantially a statement of periodicity of properties with increase of atomic weight. Newland's Law of Octaves, 1864, an arrangement of the elements in groups of eight bringing with each eighth element a repetition of properties like the eighth note of an octave in music, aroused much ridicule and little respect, though essentially the correct formulation of periodicity. It is noteworthy to record that, had Ramsay's discovery of the rare gases of the atmosphere preceded this formulation, the analogy with the musical octave would have been lost; the scoffers would have lacked one of their principal weapons of ridicule. Mendeleeff in 1869 established the same periodicity of properties by arranging the elements in the order of increasing atomic weights. His historic association with the law arises because he employed the periodic law, so discovered, as a powerful instrument of chemical classification and a weapon for prosecuting chemical research.

> "When I arranged the elements," he wrote, "according to the magnitude of their atomic weights, beginning with the smallest, it became evident that there exists a kind of periodicity in their properties. I designate by the name periodic law the mutual relations between the properties of the elements and their atomic weights; these relations are applicable to all the elements and have the nature of a periodic function."

Simultaneously, Lothar Meyer in Germany was evolving the same generalization. Meyer was more concerned with the periodic variation in the *physical* properties of the elements as a periodic function of the atomic weights of the elements, his graph of atomic volume plotted against atomic weight demonstrating the same broad periodic relationship which we may now detail as the result of the application of the Mendeleeff principle.

The accompanying table embodies the ideas as laid down by Mendeleeff with the modifications introduced by newer and better data than were available to Mendeleeff and modified also by the additions—especially that of Group O, which comprises the rare gases of the atmosphere—which subsequent

TABLE I

THE PERIODIC TABLE

Periods		Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Formula of highest oxide Formula of hydride		— —	R_2O RH	RO RH_2	R_2O_3 RH_3	RO_2 RH_4	R_2O_5 RH_3	R_2O_6 RH_2	R_2O_7 RH	RO_4 —
First short period		He *2* 4.00	H *1* 1.008 Li *3* 6.94	Be *4* 9.1	B *5* 10.9	C *6* 12.00	N *7* 14.01	O *8* 16.00	F *9* 19.0	
Second short period		Ne *10* 20.2	Na *11* 23.00	Mg *12* 24.32	Al *13* 27.1	Si *14* 28.3	P *15* 31.04	S *16* 32.0	Cl *17* 35.46	
First long period	Even Series	A *18* 39.9	K *19* 39.1	Ca *20* 40.07	Sc *21* 45.1	Ti *22* 48.1	V *23* 51.0	Cr *24* 52.0	Mn *25* 54.93	Fe *26* Co *27* Ni *28* 55.84 58.97 58.68
	Odd Series		Cu *29* 63.57	Zn *30* 65.37	Ga *31* 70.1	Ge *32* 72.5	As *33* 74.96	Se *34* 79.2	Br *35* 79.92	
Second long period	Even Series	Kr *36* 82.92	Rb *37* 85.45	Sr *38* 87.63	Y *39* 89.33	Zr *40* 90.6	Cb *41* 93.1	Mo *42* 96.0	— *43*	Ru *44* Rh *45* Pd *46* 101.7 102.9 106.7
	Odd Series		Ag *47* 107.88	Cd *48* 112.4	In *49* 114.8	Sn *50* 118.7	Sb *51* 120.2	Te *52* 127.5	I *53* 126.92	
Third long period	Even Series	Xe *54*	Cs *55* 132.81	Ba *56* 137.37	La *57* 139.0	Ce *58* 140.25				
	Odd Series	130.2		The Rare Earth Elements Pr *59* to Yb *71*						
Fourth long period	Even Series					Ct-Hf *72* ca. 179	Ta *73* 181.5	W *74* 184.0	— *75*	Os *76* Ir *77* Pt *78* 190.9 193.1 195.2
	Odd Series		Au *79* 197.2	Hg *80* 200.6	Tl *81* 204.0	Pb *82* 207.2	Bi *83* 208.0			
Fifth long period		Rn An *86* Tn 222	— *87*	Ra *88* 226	Ac *89*	Th *90* 232.15	UX_2 *91*	U *92* 238.2		

research and discovery have permitted. For convenience in subsequent discussion, the table has been amplified by the insertion of the atomic numbers of the elements as well as the atomic weights. The table is in its essentials, however, identical with that of Mendeleeff. It contains 9 vertical columns or groups and 12 horizontal rows termed series or periods. Hydrogen is in a series by itself. It possesses the properties of the elements of Group I in certain of its compounds, that of Group VII in others.[1] Following hydrogen come two *short periods* of eight elements each, falling naturally into the eight groups from Group O to Group VII, helium to fluorine in the first of these two series, neon to chlorine in the second. Beyond chlorine, the next thirty-six elements fall naturally on the basis of properties into two groups of eighteen, the two first *long periods*, argon to nickel in the first, krypton to palladium in the second. These groups of eighteen show a variation from the two short periods in that three elements in each period, so called transitional elements, iron, cobalt, nickel and ruthenium, rhodium and palladium are grouped together in Group VIII. This arrangement was devised by Mendeleeff as a result of obvious difficulties in placing them in other groups and by reason of their close similarity one to another. By the arrangement indicated, krypton and xenon come into Group O with the other rare gases. The other members of the various groups fall naturally into the classification on the basis of similarity of properties. Mendeleeff arranged the remaining elements in three *long periods* in which there were many gaps, but in which the similarity of chemical and physical properties provided a sure guide for allocation. It is now known, as will be later discussed in detail, that, following the second period of eighteen comes a longer period of thirty-two elements of which the initial element is xenon, the last element platinum. This long period is succeeded by an incomplete fragment, seven in number, two of which are yet undiscovered, of which the initial element is the emanation of radium, a gas of the rare gas type, and of which the heaviest known element, uranium, is the last member of the series in so far as they have been discovered. The first long period of thirty-two elements contains a trio of similar elements, osmium, iridium and platinum, as in the groups of eighteen, these being assigned likewise to Group VIII. The rare earth elements are also members of this long period of thirty-two.

The Mendeleeff arrangement brings together, in one group, elements which have general family properties, physical and chemical, which vary gradually from first to last and which resemble one another more closely than do any of the other elements. This similarity and gradual variation suggests some common feature of internal construction or architecture. In the series, or horizontal lines of the table, there is a marked difference from member to member in physical and especially in chemical properties. Thus, for example in the matter of maximum oxide forming capacity, the variation of a series is from an element with no power of combination, the rare gas, through elements with respective oxides R_2O, RO, R_2O_3, RO_2, R_2O_5, R_2O_6, R_2O_7 and in some cases R_2O_8. Each series, however, more or less resembles the series which preceded it, with one proviso. In the long periods there are two series, the so-called 'odd' and 'even' series. Examination will show that the 'even' series 4, 6 and 8 resemble one another, 5 and 7 also, much more so than do the 'even' series resemble the 'odd.' On the basis of indivisible atoms this factor receives no elucidation. It was merely observed and accepted in the original classification. The explanation must be sought and, as will be shown, is found in the architecture of the atom. As observed above with the oxides, the maximum state of oxidation progressively increases from left to right in a series. It should be observed also that the elements show a minimum valency in hydride formation, rising from 0 to 4 as we pass from a rare gas such as helium to a member of Group IV such as carbon. Beyond Group IV, however, the combining power falls as indicated by the compounds NH_3, OH_2, FH. This factor also lacked elucidation in the original formulation of the periodic law.

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[1] H_2O—Na_2O; HCl—$NaCl$; $LiCl$—LiH. See: Peters, *Z. anorg. allgem. Chem.*, **131**, 140 (1923). Bardwell, *J. Am. Chem. Soc.*, **44**, 2499 (1922).

The Applications of the Periodic Law: As pointed out by Mendeleeff the periodic law could be employed in. (1) The classification of the elements; (2) The estimation of atomic weights; (3) The prediction of properties of unknown elements; (4) The correction of atomic weights.

(1) In the classification of the elements the periodic arrangement has never been surpassed nor superseded. It is still a most useful and convenient method of classifying the data of inorganic chemistry whether of elements or of compounds.

(2) Mendeleeff assigned to indium an atomic weight of 113.4 on the basis of Winkler's value of 37.8 for the equivalent weight, this makes indium tervalent, gives it place in Group III of the table between cadmium and tin, below gallium, where it fits very well. Specific heat measurements of indium metal confirmed the correctness of this assignment.

(3) Mendeleeff used the table to predict the properties of missing elements in Group III and Group IV akin to boron, aluminium and titanium. The predictions concerning eka-boron, eka-aluminium and eka-silicon were abundantly justified and confirmed in the subsequent discoveries of scandium, gallium and germanium respectively.

(4) Mendeleeff predicted corrections in the atomic weights of osmium, iridium and platinum which gave to them this order rather than that given by the order of atomic weights accepted in 1870 which would have given platinum, iridium, osmium The periodic law has not, however, always been the successful guide in corrections to accepted atomic weights as will now be discussed.

The Defects of the Periodic Law: On placing elements in the order of atomic weights two outstanding anomalies presented themselves to Mendeleeff. Tellurium, being assigned an atomic weight greater than that of iodine, would have passed into the halogen group, while iodine would have been placed in the oxygen, sulphur, selenium group. This would have been an obvious inversion of the periodicity of properties. Since the atomic weight of iodine had been many times checked and rechecked, so that considerable certainty could be attached to its value, Mendeleeff suggested that the atomic weight of tellurium must be wrong, that the correct value would be between 123 and 126 instead of the then accepted value of 128. Hence ensued a vigorous study of tellurium, its purity, purification and atomic weight determination. Efforts were made in abundance to separate therefrom some constituent of higher atomic weight which would have a position below tellurium in the 6th group.

All these efforts were fruitless. A multiplicity of methods of purification all failed to yield a tellurium of atomic weight lower than that of iodine. The exception did not nullify the periodic law. The wonderful truth and value of the periodic relation were abundantly evident. As a consequence, and until the reason for the anomaly should reveal itself, tellurium and iodine were assigned to those group positions to which their properties, chemical and physical, indicated that they belonged, order of atomic weights notwithstanding.

Cobalt (58.97) and nickel (58.68) were similarly misplaced on the basis of order of atomic weights. The sequence from the standpoint of properties of the first three transitional elements is most certainly iron, cobalt, nickel, whereas the order of atomic weights is iron, nickel, cobalt. Again, the presence of another element, 'gnomium,' was suspected. Again, intensive and painstaking labors failed to reveal the element or reverse the order of atomic weights. Cobalt and nickel likewise remained anomalous.

One other pair of misfits arose with the discovery of the rare gases by Ramsay. Argon of atomic weight 39.88, an obvious member of Group 0, was found to have an atomic weight greater than that of potassium, 39.10, again obviously a member of Group I. In view of these anomalies in the face of such overwhelming evidences of the approximate truth of the law in the majority of its details it is little wonder that Ramsay asked "Why this incomplete concordance?" The answer has emerged and in the unfolding of the mystery the student of chemical philosophy has much to learn. He will find an answer to the query of Ramsay. The incomplete concordance is evidence of the limitations to which many laws are subject, is evidence that the laws in question are but *approximations* to the fundamental law. The incomplete concordance is evidence of incomplete truth. The realization of this will be valuable, for it will give to authentic exceptions to general laws a vital importance in the search for truth. Science is full of illustrations of this fact. The exceptions to the Law of Dulong and Petit were an index of the approximate truth only of the law. It will be shown later that they constituted a sign post to a more fundamental law of the specific heats of elements of which Dulong and Petit's Law is but a limiting case. Ramsay himself found in the anomalous density of nitrogen from air and from nitrogen compounds as determined by Lord Rayleigh the sign post to a whole group of chemical elements at that time unknown. The anomalies in the periodic law were the arrows pointing to the necessity of obtaining yet more fundamental truths concerning the nature, the architecture and the periodic relationships of elementary matter. As the science progressed new sign posts appeared. The allocation of the rare earths to positions in the periodic table was a problem in itself of great complexity. The discovery of the radio-elements multiplied the difficulties of allocation. These difficulties gave to other less pronounced difficulties an added significance. Thus, for example, the problem of the odd and even series recurs. Copper, silver and gold are distinct variants from the alkali elements. Gold chloride, $AuCl_3$, seems out of place in the compounds of the elements of Group I. Lead resembles thallium, mercury is similar to copper. Magnesium behaves like manganese in some of its compounds. In the ultimate solution, such problems will find their elucidation.

The Periodic Law and Electrochemistry: Faraday concluded that the laws of electrochemical action which he deduced were consonant with the facts of the atomic theory. Subsequent researches of Grove, Clausius, Hittorf, and Arrhenius established that, in conducting solutions, the elementary constituents were present, not as atoms, but as charged ions. It is of interest to examine the nature of these postulated ions in terms of the Mendeleeff classification. In a simple solution of an electrolyte, say of sodium chloride, the ionic theory postulated the presence of positively charged sodium ions and negatively charged chloride ions

$$\text{NaCl} + aq = \text{Na}^{++}_{aq} + \text{Cl}_{aq}.$$

With an electrolyte such as barium chloride the solution contained barium ions with a doubly positive charge and twice the number of singly charged negative ions

$$\text{BaCl}_2 + aq = \text{Ba}^{++}_{aq} + 2\text{Cl}^{-}_{aq}.$$

With sodium sulphide on the other hand the opposite distribution of charges was postulated

$$\text{Na}_2\text{S} + aq = 2\text{Na}^{+}_{aq} + \text{S}^{--}_{aq}.$$

Similarly, aluminium chloride dissociates thus:

$$\text{AlCl}_3 + aq = \text{Al}^{+++}_{aq} + 3\text{Cl}^{-}_{aq}.$$

In terms of electrochemical theory, therefore, the elements of Group I yield univalent positive ions, Group II divalent positive ions, Group III trivalent positive ions. Group VII contains the elements yielding univalent negative ions, Group VI elements yielding divalent ions, Group V the trivalent negative ions, though these are rare. On the left of Group IV are to be found the pronouncedly electro-positive elements, to the right the more pronouncedly electronegative compounds. These facts are of importance in the ensuing development of atomic structure. They provide a background from which to approach the newer ideas.

Atomic Structure: The atomic theory of Dalton provides, as has been shown, a satisfactory basis for the laws of chemical combination and the atomic weight provides a useful, if not completely satisfactory, basis for the classification of the elements. The concept of definite and indivisible atoms, of different weights, could not, however, be the ultimate solution of the problem of material structure. It provides no answers to a variety of problems. The difference in chemical properties between two atoms, say hydrogen and oxygen, can never be satisfyingly relegated to a simple difference in weight. Wherein does the difference in weight lie? What factors determine the weight difference? Furthermore, a number of physical and chemical properties of elementary substances cannot be explained upon any basis of weight variation of ultimate indivisible particles. The varying valence of the different elements and also the varying valences of a single element remain entirely unexplained on the basis of the simple atomic theory. The spectral differences among the elements are likewise unexplainable. As has already been emphasized, the similarity and periodicity of properties, both physical and chemical, is the strongest possible evidence that like elements must possess similarities of architecture not envisaged by a theory of indivisible atoms. The inadequacies of the periodic system of classification are further sign posts indicating the need for further exploration of the composition of the individual atoms. Dalton had a glimpse from whence progress might come, for in his address to the Royal Society, upon receiving the Royal Medal he stated:

> "The causes of chemical change are as yet unknown, and the laws by which they are governed; but, in their connexion with electrical and magnetic phenomena there is a gleam of light pointing to a new dawn in science."

The Electron: It is of interest to note that the development of the concept of atomic structure commenced when the concept of atomic electricity received its first quantitative study. Faraday's experiments on the conduction of salt solutions are the first experiments indicative of discreet units of electricity. G. Johnstone Stoney in an address before the British Association in 1874, published in 1881,[1] definitely emphasizes this fact.

> "Nature presents us with a single definite quantity of electricity which is independent of the particular bodies acted on. To make this clear, I shall express Faraday's Law in the following terms, which, as I shall show, will give it precision, viz.: For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte which is the same in all cases."

Helmholz in the Faraday lecture at the Royal Institution in 1881 emphasized the same point of view:

> "Now the most startling result of Faraday's Law is perhaps this, if we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity."

G. Johnstone Stoney, 1891, gave to the 'natural unit of electricity,' thus defined in reference to Faraday's Law, the name 'electron.' Faraday's Law, however, was not sufficient to establish the atomistic concept of electricity. It applied only to solutions of electrolytes. Metallic conduction was still discussed in terms of 'ether strains' and 'continuous homogeneous fluids.' The proof of atomic electricity did not come until the mechanism of gaseous conduction had been studied and the properties of gases acted upon by X-radiation and radioactive materials had become familiar.

The experiments of J. J. Thomson and his collaborators at the Cavendish Laboratory, Cambridge, England, supplied the original information in this field. Gases treated with X-rays were found to be conducting. The conductivity thus induced in a gas was caused by an agency which could be removed by filtration through glass wool, by passage of the gas through metal tubes or between plates maintained at a sufficiently large potential difference. The conductivity was therefore due to electrically charged particles. More detailed knowledge of the nature of the charged particles was obtained by a study of the conduction of electricity through gases at low partial pressures. When currents at high potentials are discharged through gases at pressures of about 0.01 mm. or lower, charged particles or corpuscles are shot off from the cathode. These particles, first investigated by Sir Wm. Crookes, and called by him the 'fourth state of matter,' have properties the study of which led eventually to an appreciation of their importance in atomic structure. The cathode particles were shown to have the following properties:

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[1] *Phil. Mag.*, (5) 11, 384 (1881).

(1) They travel in straight lines normal to the cathode and cast shadows of opaque objects placed in their path.

(2) They are capable of producing mechanical motion

(3) They produce phosphorescence in many objects exposed to their action, e.g., blue phosphorescence in lead glasses.

(4) They produce a rise in temperature in objects which they strike.

(5) They may be deflected, by electromagnetic and electrostatic fields, from their normal rectilinear paths.

(6) The charge carried by the particles is negative since they electrify negatively insulated metallic electrodes upon which they fall

(7) They may penetrate thin sheets of metal, the stopping power of the metal varying directly with the thickness of the metal and with its density.

(8) They act as nuclei for the condensation of supersaturated vapors. The fogs thus formed are useful as a means of rendering the particles visible.

(9) The particles were identical in nature and in the ratio of charge carried to mass of the particles, *irrespective of the nature of the residual gas in the discharge tube*. This represented the first definite indication that the *cathode particles were a common constituent of all atoms.*

The Velocity of the Cathode Particle: The velocity of the particle can be determined by measuring the displacement effected by known electrostatic and electromagnetic fields on a fine pencil of cathode particles. Such a pencil of particles impinging on a phosphorescent screen may be located by the phosphorescent spot produced. If a strong magnetic field H be applied to such a pencil of rays they will be deflected from their rectilinear path. The force exerted by the field H on a particle carrying a charge e, moving with a velocity v, will be Hev. At equilibrium, this force will be equal to the centrifugal force of the moving particle acting outwards along its radius of curvature, r. Therefore, if the mass of the particle be m, the following relation holds

$$Hev = \frac{mv^2}{r} \cdot$$

Since H and r are both measurable it follows that the ratio $mv/e = Hr$ can be determined. Now, by superposing on the pencil of cathode particles thus magnetically deflected a suitable electrostatic field X, the pencil may be restored to its original rectilinear path. In such case, by equating the electrostatic and electromagnetic forces involved, there follows

$$Xe = Hev$$

whence v may be determined from the known values of X and H. Hence also the ratio e/m may be obtained.

By removing the electromagnetic field, a further check upon the value of e/m may be obtained. The electrostatic field deflects the corpuscles from their normal rectilinear path. The downward acceleration $\left(= \frac{\text{force}}{\text{mass}}\right)$ produced by the action of the electrostatic field is Xe/m. The distance through which the particle will fall in time t is

$$d = \frac{1}{2}\frac{Xet^2}{m}.$$

Now $t = l/v$ where l is the distance travelled by a particle of velocity v. Hence, the vertical displacement, d, as revealed by the change in position of the phosphorescent spot is given by

$$d = \frac{1}{2}\frac{Xe}{m}\frac{l^2}{v^2}.$$

Since d and l may be measured, X is known and v deduced as indicated above, it is possible to calculate e/m from the equation

$$\frac{e}{m} = \frac{2dv^2}{Xl^2}.$$

By these methods Thomson was able to show that the ratio e/m was constant for all cathode rays, irrespective of the nature of the electrodes or the nature of the residual gas in the discharge tube for all velocities of travel not approaching the velocity of light. The average value of v was found to be 2.8×10^9 cm. per second. The value of e/m in such discharge tubes was approximately 1.79×10^7 electromagnetic units. This may be compared with the ratio of e/m for a hydrogen ion. It was known that the charge carried by such an ion is 4.77×10^{10} electrostatic units. The mass of a hydrogen ion is 1.64×10^{-24} grams. Hence in electromagnetic units, the charge e/m for a hydrogen ion is

$$\frac{4.77 \times 10^{-10}}{1.64 \times 10^{-24} \times 3 \times 10^{10}} = 0.97 \times 10^4 \text{ electromagnetic units.}$$

For the cathode particle therefore the ratio e/m is approximately

$$\frac{1.79 \times 10^7}{0.97 \times 10^4} = 1845 \text{ times}$$

greater than that for the hydrogen ion. It is apparent that one of several factors may account for this: (1) either the charge on the particle is some 1845 times greater than that on the hydrogen ion, the masses being identical, or (2) the mass of the particle may be 1/1845 of the mass of the hydrogen ion and the charges identical or (3) the cathode particle may differ in both charge and mass from that of the hydrogen ion. It will now be shown that the charge of the cathode particle is identical with that of the hydrogen ion and that, therefore, the mass of the cathode particle is approximately 1/1845 of the hydrogen ion.

The Charge Carried by a Cathode Particle: The earliest efforts to determine e were made by Townsend,[1] J. J. Thomson[2] and H. A. Wilson.[3] Townsend produced his charged particles by electrolysis of solutions at high current densities. The gases thus evolved contain a small fraction of the molecules in the charged condition. When these charged gases were bubbled through water they formed a cloud or fog which could be discharged by bubbling through concentrated sulphuric acid. The removal of the moisture in this manner did not entirely destroy the charge on the gas. Repetition of the procedure would give new clouds. Townsend assumed that the number of ions was the same as the number of fog particles. He determined the total electric charge per cubic centimeter carried by the gas. He determined the total weight of the cloud by absorbing the water in sulphuric acid. He found the average weight of the water droplets by observing their rate of fall under gravity, computing their mean radius by the application of Stokes' law,

$$v = \frac{2}{9}\frac{gr^2d}{\eta},$$

where v is the velocity of fall of a drop of water of radius r and density d, falling through a gas of viscosity η, under the acceleration of gravity g. From these data Townsend computed the number of droplets, assumed equal to the number of ions, and hence the average charge carried by each ion. His mean determinations gave $e = 3 \times 10^{-10}$ electrostatic units.

Thomson's method was similar to Townsend's but utilized the observation of C. T. R. Wilson that the sudden expansion and consequent cooling of the air in the ionization vessel gave a convenient method of producing the cloud formation. The ionization was produced by means of X-rays which give rise to negative particles or ions and positive particles which are the residues from which the corpuscles have been removed. By adjusting the degree of supersaturation, condensation may be confined to the negative particles as was demonstrated by H. A. Wilson. Thomson obtained his measurement of total charge carried by the cloud by determination of the current carried by the cloud under the influence of a weak electromotive force. Thomson weighed the cloud produced and utilized Stokes' Law as in Townsend's work. As a final value for e Thomson gave $e = 6.5 \times 10^{-10}$ (1898). Later work[4] with radium as the source of ionization gave him the result 3.4×10^{-10}.

Thomson's mode of experimentation was modified by H. A. Wilson who studied the rate of fall of the cloud under gravity alone and also under the combined action of gravity and an electrostatic field. The ratio of the velocities, v_1 and v_2, under gravity alone and with the combined action of gravity and an electrostatic field X is given by the equation

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[1] *Proc. Camb. Philos. Soc.*, **9**, 244 (1897).

[2] *Phil. Mag.*, **46**, 528 (1898).

[3] *Phil. Mag.*, **5**, 429 (1903).

[4] *Phil. Mag.*, (6) **5**, 354 (1903).

$$\frac{v_1}{v_2} = \frac{mg}{mg + Xe}.$$

Combining this with Stokes' Law for v_1

$$v_1 = \frac{2}{9}\frac{gr^2d}{\eta}$$

and eliminating m by the expression $m = 4/3\ r^3d$, Wilson obtained the expression

$$e = \left\{ \frac{4}{3}\pi \left(\frac{9\eta}{2g} \right)^{3/2} \right\} \frac{g}{X} \frac{(v_2 - v_1)}{d^{1/2}} {v_1}^{1/2}.$$

This yielded for e a mean value of 3.1×10^{-10} electrostatic units. The deviations were considerable, the extreme values being 2.0×10^{-10} and 4.4×10^{-10} E.S.U. Wilson's method eliminated the assumption as to the equality of the number of droplets and the number of ions. It involved the assumption, however, that successive cloud formations gave equally sized droplets, an assumption which later work by Millikan could not be found to sustain with any certainty.

Millikan's first work with Begeman was essentially a repetition of the H. A. Wilson method using radium as the ionizing agent and a 4000 volt storage battery to charge the plates. The results were more consistent than Wilson's and gave as the mean of the observations, varying between 3.66×10^{-10} and 4.37×10^{-10}, a value $e = 4.06 \times 10^{-10}$ E.S.U.[1]

Millikan's 'balanced-drop' method.[2] This represents a distinct advance on the H. A. Wilson method. To eliminate errors due to evaporation, Millikan planned to use a sufficiently strong field, to balance exactly the force of gravity on the droplets and thus maintain the top surface of the cloud stationary. Without attaining this object, he succeeded in the more important task of studying the behavior of *individual droplets*. He found they could be held suspended in the field from 30 to 60 seconds; that they carried multiple charges varying between $2e$ and $6e$. These charges were all exact multiples and therefore reveal positively the unitary nature of electricity. The ionized cloud after formation between the plates was subjected to a given potential gradient. This removes all of the cloud particles with the exception of those which have the right ratio of charge to mass to be held in suspension in the field. Observations on these droplets were made with a telescope in the eyepiece of which three equally spaced cross hairs were placed. A small section of the space between the plates was illuminated by a narrow beam of light suitably freed from its heat rays by three water cells in series. The cross hairs were set near the lower plate and as soon as a stationary drop was found somewhere above the upper cross hair it was watched for a few seconds to make sure that it was not moving. The field was then thrown off and the plates shortcircuited. The drop was then timed in its fall by means of a stop-watch as it passed across the three cross hairs. It will be seen that this method furnishes a check upon evaporation; for, if the drop is stationary at first it is not evaporating sufficiently to influence the readings; if it begins to evaporate before the readings are completed, the time required to pass through the second space should be greater than that required to pass through the first space. In general this was not the case.

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[1] *Phys. Rev.*, **26**, 198 (1908).

[2] *Phil. Mag.*, **19**, 209 (1910).

The preceding equation of the Wilson method, applied to the balanced droplet, assumes the form

$$e = 3.422 \times 10^{-9} \frac{X}{g} (v_1)^{3/2}.$$

For, in this case, X is negative in sign, since it opposes gravity, and $v_2 = 0$. The constant 3.422×10^{-10} was chosen by Millikan as most accurately representing the terms in the Wilson equation involving the viscosity of the medium and the density of the droplets. From these determinations, Millikan deduced the value $e = 4.65 \times 10^{-10}$ E.S.U., with extreme values of 4.87×10^{-10} and 4.56×10^{-10} E.S.U.

Millikan's Oil Drop Method:[2] This later method of Millikan's represents the most accurate method of determination of the unitary quantity of electricity disclosed by the previously mentioned investigation. A diagram of this apparatus is appended. The droplets investigated were introduced into the chamber D by means of the atomizer A in the form of a finely divided spray. Eventually one of these droplets finds its way through the aperture, p, into

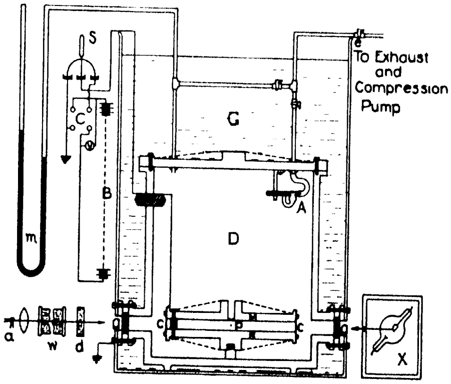

FIG. 1. Millikan's Oil Drop Apparatus

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[2] *Phys. Rev.*, 2, 143 (1913).

the space between the condenser plates, M and N. The hole p is then closed and the air between the plates ionized by a source of X-rays, X. Illumination is secured from the arc lamp, a, the heat rays being removed in filters w and d. The motion of the illuminated droplet is observed through a microscope fitted with an engraved scale. By collision with ions of the air the droplet acquires an electric charge, and then moves between plates M and N in a direction governed by the sign of the acquired charge and with a speed indicative of the sign of the charge carried. By reversal of the sign of the charge on M and N the direction of motion of the droplet can be reversed. In this way the droplet could be kept travelling back and forth between the plates. As a mean of 17 determinations of the times which the droplet required to fall between two fixed cross hairs in the observing telescope, whose distance apart corresponded to a distance of fall of 0.5222 cm., a value of 13.595 seconds with a maximum deviation of ± 0.2 sec. was obtained. When rising under the influence of an electric field produced by applying a potential difference of 5051 volts, the successive times required varied in the following way: 12.5, 12.4, 21.8, 34.8, 84.5, 84.5, 85.5, 34.6, 34.8, 16.0, 34.8, 34.6, 21.9 seconds. It will be seen that, after the second trip up, the time changed from 12.4 to 21.8, indicating, since in this case the drop was positive, that a negative ion had been caught from the air. On the next trip another negative ion had been caught. The next time, 84.5, indicates the capture of still another negative ion. From the equation

$$\frac{v_1}{v_2} = \frac{m_d g}{Xe - m_d g} \qquad \text{or} \qquad e = \frac{m_d g}{X v_1}(v_1 + v_2),$$

where m_d is the mass of the droplet, it follows that the change in velocity produced by the acquiring of an extra charge can be given by eliminating m_d and solving the equations thus:

$$(a) \quad t = 34.8 \text{ secs. against gravity } v_1 + v_2 = \left(\frac{0.5222}{13.595} + \frac{0.5222}{34.8}\right);$$

$$(b) \quad t = 84.5 \text{ secs. against gravity } v_1 + v_2 = \left(\frac{0.5222}{13.595} + \frac{0.5222}{84.5}\right).$$

The time difference between (a) and (b) is

$$0.5222\left(\frac{1}{34.8} - \frac{1}{84.5}\right) = 0.00891 \text{ cm. per second.}$$

In this manner it was shown that successive captures of an ion effected changes in the velocity of rise against gravity respectively equal to 0.008912, 0.008911, 0.008903, 0.008883 and 0.008931 cm. per second, all of which are within 1/5th of 1 per cent of the mean value of 0.00891 cm. per second. This therefore represents the change in the sum of the speeds v_1 and v_2 caused by the capture of one ion. Relationships of this sort were found to hold absolutely without exception, no matter in what gas the droplets had been suspended or what sort of droplets were used upon which to catch the ions. Experiments were conducted over five or six hours, hundreds of ions per droplet were caught and recorded by the change of speed. Here then is direct proof that the electrical charges found on ions all have exactly the same value or else small exact multiples of that value. This is the most conclusive proof of the 'atomic' structure of electricity

From the preceding equation, with the data obtained in this study of the behavior of the oil droplets, accurate values for the ratio e/m_d could be deduced. To obtain the magnitude of the unit charge e it was necessary however to determine the mass of the droplet For this purpose Stokes' Law could be employed to determine the radius and therefore the volume and mass of the droplet. To attain in these calculations the same high degree of precision which was obtained in the velocity determinations just recorded, Millikan found it necessary to make an investigation into the limitations of Stokes' Law with variation in the medium and with variation in the droplet size. On completion of this study, which revealed the necessity of correcting Stokes' Law for inhomogeneities in the medium a correction which was finally made as an empirical function of the ratio of the mean free path of the gas molecules of the medium, l, to the radius of the droplet r Millikan derived a corrected form of the Stokes' equation from which the radius of the droplet was determined,

$$v_1 = \frac{2}{9}\frac{gr^2}{\eta}(d_d - d_m)\left(1 + A\frac{l}{r}\right)$$

in which d_d is the density of the drop, d_m that of the medium, A an empirical constant, the other terms having the same significance as given previously. In this manner, the magnitude of e was finally obtained with a degree of precision embodied in the following expression.

$$e = 4.774 \pm 0.005 \times 10^{-10}.$$

The Avogadro Constant: The determination of e with the degree of precision herein indicated gives at once a most valuable method of evaluating the Avogadro constant, the number of molecules in one gram molecule of any gas under standard conditions of temperature and pressure. This is readily achieved by combining this value of e with that obtained in electrochemical work for the value of the Faraday, the quantity of electricity necessary to liberate one gram ion of a monovalent element in electrolysis. By international agreement it has been decided that the atomic weight of silver is 107.88 and the unit of electricity expressed in electromagnetic units has been defined as the amount of electricity which will deposit from a silver solution 0.1118 gram of silver. The value of the Faraday is therefore

$$\frac{107.88}{0.1118} = 9650 \text{ electro-magnetic units}$$

or, in electrostatic units, $9650 \times 2.9990 \times 10^{10}$ E.S.U. This quantity is equal to the elementary charge, e, multiplied by the Avogadro number N. Hence,

$$4.774 \times 10^{-10} N = 9650 \times 2.9990 \times 10^{10}$$

or

$$N = 6.062 \times 10^{23}$$

the precision of which is given by the expression

$$N = (6.062 \pm 0.006) \times 10^{23}.$$

The Mass of the Hydrogen Molecule: Given N, the Avogadro number, the mass of the hydrogen molecule is obtained from the molecular weight of hydrogen by simple division. The mass of the individual molecule becomes

$$\frac{2.016}{6.062 \times 10^{23}} = (3.324 \pm 0.004)10^{-24} \text{ gram.}$$

The Mass of the Electron: Millikan's work established the identity of the charges on an electron and a monovalent ion. It is evident therefore that the masses of the hydrogen atom and the electron must be in the same ratio as the respective ratios e/m and E_{H^+}/M_{H^+} bear to one another. As has already been shown, these ratios are in the ratio of 1 to 1845. Hence the mass of the electron becomes

$$\frac{1.662 \times 10^{-24}}{1845} = 9.0 \times 10^{-28} \text{ grams.}$$

It should be observed that this mass applies only to such electrons as are moving slowly relative to the velocity of light, which is true of electrons produced in the experiments on the discharge of electricity through gases. As the velocity increases, the mass becomes correspondingly greater; when the corpuscle attains the velocity of light its mass, theoretically, is infinite. Swiftly moving particles, products of radioactive decay, are known with over 90 per cent of the velocity of light, and the variation of the mass of the negative electron with speed agrees accurately with the rate of variation computed on the assumption that this mass is all of electromagnetic origin.

Mechanism of Ionization of Gases: The early work of Townsend, previously discussed, together with his measurements on the diffusion coefficients and the mobilities of the gas ions produced in his experiments, led him to the conclusion that both positive and negative ions carry unit charge. Some later data of Townsend suggested that the positive ions were possibly doubly charged.

Experiments of Franck and Westphal,[1] analogous to those of Townsend, led to the conclusion that all the negative and the majority of the positive ions carry unit charge. A small fraction, about 9 per cent, of the positive ions appeared to be doubly charged when X-radiation was the ionizing medium. With α, β and γ rays from radioactive sources they found no evidence of doubly charged ions.

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[1] *Verh. deutsch. phys. Ges.*, March, 1909.

Millikan and his co-workers have repeated the studies of the mechanism of ionization, employing the technique developed in the work detailed in the preceding sections. The conclusions to which this study led may be summarized in the following way:[1]

(1) The action of ionization by β-rays seems to consist in the release, without any appreciable energy, of one single electron from an occasional molecule through which the β-ray passes. The faster the β-ray the less frequently does it ionize.

(2) The act of ionization by X-rays or light seems to consist in the hurling out, with an energy that may be very large, but which depends on the frequency of the ether wave, of one single electron from an occasional molecule over which this wave passes.

(3) The act of ionization by rapidly moving α-particles consists in the shaking loose of one single electron from the atom through which it passes; a slow moving positive ray appears in some cases to be able to detach several electrons from a single atom.

This last conclusion is abundantly verified by the recent studies of J. J. Thomson and of Aston on the positive rays. Mass-spectrographic data reveal abundant evidence of multiply-charged atomic masses.

Ionization may result from chemical action as well as by means of the physical agencies already considered. There is a growing body of evidence indicating the presence of ions in reacting gaseous systems, persistent even when excessive precautions to exclude ion-producing mechanisms of a physical nature are excluded. Pinkus has reported[2] ionization in certain gas reactions. Recent work by Brewer and Daniels[3] demonstrates ionization in the interaction of nitric oxide and oxygen, a reaction for which Pinkus previously obtained negative results. The later work indicates definite though small ionization, of the order of 10^{-14} amperes for the oxidation of 50 cc. of nitric oxide per minute reacting in a field of 450 volts per cm. This corresponds to about one ion for every million molecules reacting.

This evidence, therefore, points undoubtedly to an atomic architecture in which the neutral atom is built up of negative electrons and positive rests or nuclei.

Size of the Electron: Assuming that the mass of the electron is entirely of electromagnetic origin, the size of the electron can be calculated from the equation

$$m = \frac{2}{3}\frac{e^2}{a},$$

which relationship connects the mass, m, with the charge e carried by a sphere of radius a. Solving this equation for a with the accepted values for m and e, the radius of the sphere over which the mass must be distributed proves to be

$$a = 2 \times 10^{-13}\,\text{cm}.$$

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[1] Millikan, The Electron, pp. 140, 141.

[2] *J. Chem. Phys.*, 18, 366, 412 (1920).

[3] *Trans. Am. Electrochem. Soc.*, Oct. 1923.

It is of importance to note that this is an entirely lower order of magnitude than the atomic radius which approximates to 10^{-8} cm. (See Chapters III and V.)

Size of the Positive Nucleus: There is no direct experimental justification for the assumption that the mass of the nucleus is entirely of electromagnetic origin. If this were so however, it is evident that, since the mass, m, of the hydrogen nucleus is 1845 times as large as that of the electron, the radius a of a hydrogen nucleus, with the mass assumed to be of electromagnetic origin, would be 1/1845 that of the electron or, approximately, 1×10^{-16} cm.

From these considerations, it is evident that the hydrogen atom would consist of a minute speck of positive electricity relatively remotely distant from a negative electron, 1845 times larger in radius, these two charged specks occupying positions within the atom the linear dimensions of which would be respectively about 1×10^{-8} and 2×10^{-5} of that of the atom. The hydrogen atom therefore could literally be said to be two tiny specks of charge in almost an infinity of space.

Proof of the minuteness of the atomic nucleus is obtainable by a study of the tracks of α-particles and β-particles through gases. Photographs of such tracks are obtainable, for the gas through which the particles travel is ionized and the ions may be rendered visible by the condensation of water vapor upon them.[1] Study of photographs so obtained shows that a β-particle may pass through as many as 10,000 atoms before it comes near enough to an electronic constituent of any of the atoms to detach it from its system and form an ion, a circumstance which indicates the relative freedom of the atomic space from such electronic constituents. Furthermore, α particles, owing to their great mass relative to the electron (approximately 7000 : 1), are uninfluenced by the electrons with which they come in contact. They may however be stopped or deflected by the more massive positive nuclei of the atoms through which they pass. Photographs reveal, however, that, on an average, an α-particle goes through 200,000 atoms without approaching near enough to the nucleus to suffer appreciable deflection. The conclusion seems inescapable therefore that the positive nucleus is also but a minute fraction of the total atomic volume.

The Nuclear Atom: The facts thus ascertained with regard to the components of the atom have led Rutherford to the formulation of the nuclear atom theory.[1] According to Rutherford an atom consists of a heavy minute positively charged nucleus surrounded by electrons probably situated to the nucleus somewhat as the planets are situated to the sun. The number of electrons outside the nucleus is equal to the net positive charge on the nucleus.

Rutherford,[2] Geiger and Marsden[3] by studies of the deflections suffered by α-particles in passing through various metal foils were able thence to calculate the number of free positive charges on the metal atoms through which the α-particles passed. They concluded that the number of free positive charges was approximately equal to half the atomic weight. This conclusion was in striking agreement with earlier work by Barkla[1] on the scattering of X-rays. This work indicated that, in each atom, the number of scattering centers, namely, the electrons, was approximately equal to one half the atomic weight. Evidence, therefore, was available with both positive and negatively charged portions of the atom as to this relationship between atomic weight and electrical charge.

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[1] C. T. R. Wilson, *Proc. Camb. Phil. Soc.*, **9**, 333 (1897), *Phil. Mag.*, **7**, 681 (1904).

[2] *Phil. Mag*, **21**, 669 (1911).

[3] *Phil. Mag.*, **25**, 604 (1913).

The Atomic Number: The actual count, with precision, of the extra-nuclear electrons in elementary substances was accomplished by Moseley, 1914.[2] The suggestion of Laue, 1912, that the regular spacing of atoms in a crystal could be utilized, on the principle of a grating, for the analysis of short wave-length ether waves, had been translated into actual practice by the Braggs,[3] an X-ray spectrometer devised and the wave lengths of various X-rays determined. Moseley, in 1914, utilizing a wide variety of elements as targets in the X-ray bulb, found that, in addition to general X-radiation which all emitted, each element emitted X-radiations characteristic of the given element. Moseley showed that the square root of the frequency (inverse wave length) of a given series of the characteristic X-ray spectra of the elements constituted an arithmetical progression; the order of increasing frequency was that of the elements arranged in the order of their atomic weights with conspicuous and significant exceptions. A missing element in the periodic order gave a missing step in the increment of the square root of the frequency In the whole series of elements ranging from hydrogen = 1 to uranium = 92, five such gaps were found indicating that five elements were still unknown in this interval. One of these, No. 72, has since been found (Celtium-Hafnium).[4] Since the X-ray frequencies involved in Moseley's investigations are probably due to vibrations arising from electrons proximate to the nucleus, the additivity of the square-root of the frequency, observed by Moseley, indicates or suggests that the charge on the nucleus in a given element differs from that of the nucleus of the preceding element in the periodic classification by a constant and definite charge.

Radioactive Disintegration and Atomic Structure: Confirmation of this conclusion from Moseley's work came from study of radioactive decay in its relation to periodic classification. As knowledge of the properties of the elements formed in the successive stages of radioactive decay became more complete, it emerged that the loss of α-particles and β-particles by a radioactive element corresponded to a definite shift of the group classification of the elements produced in the process of decay The loss of an α-particle in *every* case produced a shift, two groups to the left in the periodic table. Thus Radium (Group II) loses an α-particle to give Radon (Ra. Emanation) Group 0. Similarly loss of a β-particle gives rise to a shift of one group to the right in the periodic table. The change of Radium B, Group IV to Radium C, Group V is one illustration of such change (see, in addition, Chapter XXI). This important generalization is shared by several investigators: notably Soddy,[1] Fleck,[2] Russell[3] and Fajans.[4] Now, since the α-particle is a helium nucleus carrying a double positive charge and since the β-particle is none other than an electron, and since, moreover, these particles are certainly ejected from the nucleus, it follows that the difference between the nuclei of successive atoms in neighboring groups of the periodic table consists in the extra unit of positive charge which the heavier nucleus possesses. The atom itself being electrically neutral, it therefore follows that the extra-nuclear electrons must increase by one as the atomic table is ascended. The progressive variation in the square root of the frequency of the characteristic X-radiation as discovered by Moseley is therefore paralleled by a progressive increase of net positive nuclear charge and of extra-nuclear electrons.

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[1] *Phil. Mag.*, **21**, 648 (1911).

[2] *Phil. Mag.*, **26**, 1024 (1913), **27**, 703 (1914).

[3] X-rays and Crystal Structure, 1915.

[4] For a summary of the discussion concerning No. 72 see. *Chem. and Ind.*, **42**, 784 (1923).

Upon this basis, the assumption is natural that the hydrogen atom consists of a proton or unit positive charge of mass = 1 and a negative electron. The helium nucleus on this basis will be composed of four protons with two nuclear electrons giving the nucleus a net positive charge of two, requiring two extra-nuclear electrons to complete the neutral atom. Similarly, lithium nucleus will have net positive charge of 3 with three external electrons, beryllium will have 4 such, boron 5, carbon 6, nitrogen 7, oxygen 8, fluorine 9 and so on.. To the net nuclear charge or, what is the same thing, to the number of extra-nuclear electrons as revealed by the Moseley investigations, the term atomic number has been assigned. In the periodic classification given in a preceding section the atomic numbers of the elements have been given in addition to the atomic weights.

The Atomic Number and Defects in the Periodic Table: It was shown that on the basis of weight classification certain definite transpositions of the elements would occur which would not be in harmony with the periodicity of properties shown by the bulk of the elements when arranged on a weight basis. The transposition of argon and potassium, of tellurium and iodine and of cobalt and nickel was noted. When studied by the Moseley method, the order of the square root of the characteristic frequencies of these elements was such as would be anticipated on the basis of properties and not that obtained on the basis of atomic weight. Argon therefore has an atomic number of 18, potassium 19, cobalt 27, nickel 28, tellurium 52, iodine 53. The answer to the query of Ramsay as to the lack of complete concordance in the periodic classification was evident and revolutionary. The atomic weight is not the fundamental factor in atomic behavior. The properties of the elements are a function of their atomic architecture. Atomic weight is a secondary factor useful as a guide in the great majority of cases but at fault in the cases just mentioned and certain others now to be discussed.

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[1] Chemistry of the Radio Elements, Part II, p. 2, 1914; *Chem. News*, **107**, 97 (1913).

[2] *J. Chem. Soc.*, **103**, 381, 1052 (1913).

[3] *Chem. News*, **107**, 49 (1913).

[4] *Physikal. Z.*, **14**, 49, 131, 136 (1913).

Isotopes: The existence of elements differing in mass yet identical in chemical properties was made familiar by the study of radioactive decay. It gradually emerged that the end product in the decay of radium was Radium G, radio-lead, identical in chemical properties with that of ordinary lead. Moreover, as the change in group classification brought about by loss of α- and β-particles became understood, it was further evident that Radium B, Radium D and Radium G were all members of Group IV in the periodic classification. This is evident from the accompanying chart. Furthermore, since loss of an

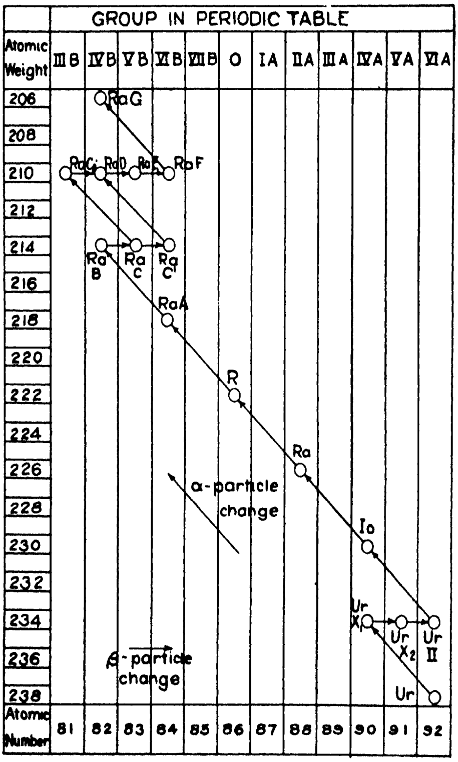

FIG. 2. Radium Disintegration Series

α-particle (helium nucleus) results in a diminution in the atomic weight by four units, while the β-particle change is without influence on the weight, it is evident that, by calculation of the α-particles lost in the successive changes, the atomic weights of successive products could be deduced from that of radium. Assuming an atomic weight of 226 for radium, that of Ra B becomes 214 (3 α-particles lost), that of Ra D becomes 210 (4 α-particles lost), and Ra G becomes 206 (5 α-particles lost). All these elements have properties identical with those of ordinary lead, whose atomic weight is 207.2, in all properties except those dependent upon mass. The masses differ as can be seen from the above examples by so much as eight units (206–214). The end-product of the thorium series of radioactive elements is likewise a member of Group IV analogous to lead with an atomic weight of 208.1. To such elements, identical in properties other than those dependent upon mass, the term *isotopes* was applied. The conclusions reached upon the basis of calculation from the atomic weight of lead and the α-particle loss have been abundantly confirmed by actual atomic weight determinations.[1 2 3]

The wide variety of elements produced in radioactive decay, their similarity of properties, in spite of wide differences in atomic weight, would have presented a problem of considerable complexity for periodic classification had not the Moseley discovery elucidated the true basis of classification and demonstrated the secondary importance of the weight relationship. All such isotopes while differing greatly in mass are identical in atomic number. Their net nuclear charges are identical. They have a common extra-nuclear electronic configuration. They differ only in the mass of the nucleus.

Non-Radioactive Isotopes: The existence of atoms of identical nuclear charge but differing masses, outside the range of radioactive materials, was demonstrated by the investigations of J. J. Thomson and of Aston on the properties of the positive rays from a discharge tube. In the earlier sections, a considerable discussion has been given of the electrons liberated from atoms by the action of various forms of energy. Little has been stated concerning the residues from such changes. Positive rays were discovered by Goldstein in 1886 in the discharge of electricity through gases at low pressure. Using a perforated cathode he showed that streamers of light were present behind the cathode perforations, and assumed that the light indicated the presence of rays travelling in the opposite direction from the cathode rays. From the manner of their production he termed them 'canal strahlen.' Wien[4] showed that they could be deflected by a magnetic field. The detailed investigation of their properties was undertaken by J. J. Thomson,[5] who gave to them the term Positive Rays since they were shown to carry a positive charge. The rays are produced by ionization of gases at low pressures in a strong electric field of the order of 30,000–50,000 volts. They are the residues from such ionization processes.

The method of measurement employed by Thomson to investigate the charge and mass of such rays is known as the 'Parabola' method. It consisted

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[1] Richards and Lembert, *J. Am. Chem. Soc.*, **36**, 1329 (1914); **38**, 2613 (1916).

[2] Soddy, *J. Chem. Soc.*, **105**, 1402 (1914).

[3] Hönigschmidt, *Compt. rend.*, **158**, 1796 (1914).

[4] *Verh. d. Phys. Ges.*, **17**, 1898.

[5] Rays of Positive Electricity, 1913.

essentially in allowing the rays to pass through a very narrow tube and then in analyzing the fine beam so produced by electric and magnetic field. Under the combined influence of an electrostatic and an electromagnetic field a ray will be deflected from its normal path and will strike a receiving screen at a point x, y, where y/x is a measure of its velocity and y^2/x is a measure of m/e, the ratio of mass to charge. This follows from the application of simple dynamics to the separate actions of the electrostatic field X and the electromagnetic field H since

$$x = k\left(\frac{Xe}{mv^2}\right)$$

and

$$y = k'\left(\frac{He}{mv}\right)$$

in the manner previously demonstrated for the electron. The velocity v of the rays may vary however over a considerable range. Hence, for constant m but variable v, the locus of impact of the rays with the screen will be a parabola, pp' (Fig. 3). Rays of larger mass m' yield a similar parabola of smaller magnetic displacement qq'. The displacement of the parabolas along the magnetic axis OY at a given value along the electric field gives a measure of the relative masses since

$$\frac{m'}{m} = \frac{(pn)^2}{(qn)^2}.$$

With one known parabola, the mass of all other rays can be identified.

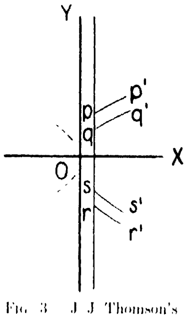

FIG. 3. J. J. Thomson's Parabola Method

The sharpness of the parabolas, obtained photographically in this way by using a photographic plate as receiving screen for the rays, established experimentally for the first time the fundamental assumption of the Daltonian atomic theory, that the atoms (in these experiments the positive rays) of the same element had the same mass.

A second method of positive ray analysis devised by Dempster[1] causes the charged particles to fall through a definite potential difference. A narrow bundle is separated out by a slit and is bent into a semicircle by a strong magnetic field; the rays then pass through a second slit and fall on a plate connected to an electrometer. The potential difference P, the magnetic field H and the radius of curvature r determine the ratio of the charge to the mass of the particle since

$$\frac{e}{m} = \frac{2P}{H^2r^2}.$$

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[1] *Phys. Rev.*, **11**, 316 (1918).

This method is essentially that used by Classen[1] for the determination of e/m for electrons.

Aston improved the technique of positive ray analysis by the use of the mass-spectrograph illustrated in Fig. 4. Positive rays are sorted out into a thin ribbon by means of two parallel slits, S_1 and S_2, and are then spread into an electric spectrum by means of the charged plates P_1 and P_2. A portion of this spectrum deflected through an angle θ is selected by the diaphragm D and passed through the circular poles of a powerful electromagnet O, the field of which is such as to bend the rays back again through an angle ϕ, more than twice as great as θ. The result of this is that rays having a constant ratio m/e will converge to a focus F. If a photographic plate is placed at GF as indicated, a spectrum dependent on mass alone is obtained.

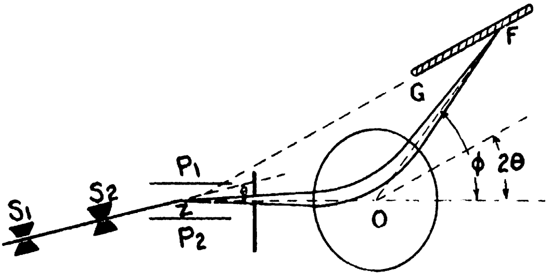

FIG. 4. Aston's Positive Ray Spectrograph

Aston has recently announced[2] his discovery of yet another method of mass analysis with the aid of which further determinations of the masses of elementary particles have been made. The most significant result of Aston's measurements is the conclusion that the lighter elements also exist as isotopes and that, with the exception of hydrogen, the weights of the isotopic elements are whole numbers within the accuracy of the experimental method, in most cases about one part in a thousand. The results of such investigations to date are embodied in the accompanying table.

Aston's discovery removes at once the only serious objection to the unitary theory of matter which, as has been previously recorded, lay in the deviations from whole numbers in the atomic weight tables. Thus, the hypothesis of Prout was hardly tenable while exact atomic weight determinations showed the atomic weight of chlorine to be 35.46. Aston's determinations reveal chlorine as a mixture of isotopic elements of masses 35, 37, and possibly 39 in such a ratio as to give an atomic weight of the mixture equal to 35.46. Similarly with the other elements deviating from the whole number rule demanded on the basis of a unitary theory.

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[1] Jahr. Hamburg. Wiss. Anst., Beiheft 1907.

[2] Brit. Ass. Liverpool, Sept. 1923. *Chem. and Ind.*, **42**, 935 (1923). *Phil. Mag.*, **47**, 385 (1924).

TABLE II

ELEMENTS AND THEIR ISOTOPES

Element	Atomic Number	Atomic Weight	Minimum Number of Isotopes	Masses of Isotopes in Order of Intensity
H	1	1.008	1	1.008
He	2	3.99	1	4
Li	3	6.94	2	7, 6
Be	4	9.02	1	9
B	5	10.9	2	11, 10
C	6	12.00	1	12
N	7	14.01	1	14
O	8	16.00	1	16
F	9	19.00	1	19
Ne	10	20.20	2	20, 22
Na	11	23.00	1	23
Mg	12	24.32	3	24, 25, 26
Al	13	26.96	1	27
Si	14	28.3	2	28, 29, (30)
P	15	31.04	1	31
S	16	32.06	1	32
Cl	17	35.46	2	35, 37
A	18	39.88	2	40, 36
K	19	39.10	2	39, 41
Ca	20	40.07	2	40, 44
Sc	21	45.1	1	45
Ti	22	48.1	1	48
V	23	51.0	1	51
Cr	24	52.0	1	52
Mn	25	54.93	1	55
Fe	26	55.84	(1)	56, (54)?
Co	27	58.97	1	59
Ni	28	58.68	2	58, 60
Cu	29	63.57	2	63, 65
Zn	30	65.37	4	64, 66, 68, 70
Ga	31	69.72	2	69, 71
Ge	32	72.5	3	74, 72, 70
As	33	74.96	1	75
Se	34	79.2	6	80, 78, 76, 82, 77, 74
Br	35	79.92	2	79, 81
Kr	36	82.92	6	84, 86, 82, 83, 80
Rb	37	85.45	2	85, 87
Sr	38	87.63	1	88
Y	39	88.9	1	89
Ag	47	107.88	2	107, 109
Sn	50	118.7	7(8)	120, 118, 116, 124, 119, 117, 122, (121)
Sb	51	121.77	2	121, 123
I	53	126.92	1	127
Xe	54	130.2	7(9)	129, 132, 131, 134, 136, 128, 130, (126), (124)
Cs	55	132.81	1	133
Hg	80	200.6	(6)	(197–200), 202, 204

The discovery of isotopes explains also the remaining defect of the periodic classification, the inversion of argon and potassium, of tellurium and iodine and of cobalt and nickel in the arrangement of elements by weight. Thus, argon with an atomic weight 39.88 has isotopes of weight 40 and 36, the former in predominating amount. Potassium has two isotopes, 39 and 41, the former also largely predominating. In nuclear charge the argon isotopes are one less than those of potassium as the Moseley investigations reveal. The relative amounts of the two isotopes in each case determine the inversion of atomic weights. The same holds true for the heavier elements tellurium and iodine, cobalt and nickel.

Isotopes have identical nuclear charge but differ in mass. The isotopes of lithium have masses 6 and 7, the latter strongly predominant, since the atomic weight is 6.94. As the atomic number of lithium is three, it follows that the nucleus of Li^6 must be composed of 6 protons[1] with 3 electrons. That of Li^7 must contain 7 protons with 4 electrons. This gives each the net positive charge of 3 required. The planetary electrons are likewise 3 in number. What the actual structure of such nuclei is has been the subject of considerable conjecture recently;[2] as yet, however, little of a definite nature is available. Two hypotheses are being considered. According to one, the nuclei of atoms consist of helium nuclei or α-particles held together so that their packing effect upon each other is small; in the case of atoms not having a mass of $4n$, additional protons and electrons are supposed to be present. According to the second hypothesis, the actual arrangement of the protons and electrons need not be at all similar to that in a helium nucleus. Evidence from radioactive studies on the disintegration of light atoms by the collision of swift α-particles seems to favor the former hypothesis. Rutherford and Chadwick have shown[3] that such collisions produce swift hydrogen nuclei from the atoms of boron, nitrogen, fluorine, sodium, aluminium and phosphorus. These atoms are elements whose masses are of the types $4n + 2$ and $4n + 3$. The effect was not obtained from atoms of the type $4n$.[4] This result suggests that in the atoms of this last type the protons are all bound in the form of helium nuclei.

The Arrangement of the Extra-Nuclear Electrons: Little can be said at this stage concerning the arrangement of the extra-nuclear or planetary electrons. Two points of view are to be satisfied in any complete theory of the electronic arrangement. On the one hand there is the demand of the physicist for a dynamically stable atom which requires the electrons to be in motion in orbits around the nucleus. The beginnings of such a theory are to be found in the Bohr theory of atomic structure. This theory of electrons rotating around nuclei has led to conspicuous success in the interpretation of the spectra of hydrogen and to some extent of helium, in the calculations of ionization potentials and resonance potentials; with its aid, the Moseley law may be predicted; it predicted a relation between the frequencies of lines in two succeeding series of characteristic X-radiation such as the K and the L series. The theory employs the quantum theory of radiation and so its detailed discussion may well be deferred until this chapter in the development of modern chemistry is presented.

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[1] Proton is the name suggested by Rutherford (Brit Ass. 1920) for the hydrogen nucleus.

[2] Harkins, *Phys. Rev.*, **15**, 73 (1920).
Rutherford, *Proc. Roy. Soc.*, **97A**, 374 (1920).
Gehrcke, *Physik. Z.*, **22**, 151 (1921).
Brosslera, *Rev. Chim.* 1, 42, 74 (1921).

[3] Rutherford and Chadwick, *Phil. Mag.*, **42**, 809 (1921).

[4] For later views, see Kirsch and Pettersson, *Nature*, **112**, 394, 687 (1923). Bates and Rogers, *Nature*, **112**, 435 (1923).

The facts of chemistry, of valence and of stereo-chemical relationships demand, on the other hand, that the valence electrons be grouped in certain positions of equilibrium about the atomic nucleus This, the chemical attitude to the problem, has given rise to static or semi-static electron configurations of which the most notable discussions are those of Lewis,[1] of Kossel[2] and of Langmuir.[3] These theories also may well be discussed in conjunction with the theory of the Bohr atom since there seems now to be a possibility of reconcilement between the two extreme viewpoints and a general theory possible[4] to cover all cases. The solution of the problem is important. The chemist cannot fail to remember that all the facts of his science, all the multitudinous compounds with which he deals, all the various properties which he assigns to his elements and compounds are, with the exception of those factors definitely related to mass and therefore to the nucleus, to be ascribed to the various permutations and combinations of the extra-nuclear electrons.

Applications of the Atomic Concept: This concept of atomic make-up of matter, as developed in the preceding sections, is the concept which is to be harmonized with the fundamental factors of theoretical chemistry. We shall see that the atomic concept is at the root of our theories of the gaseous, liquid and solid states It will be shown how the kinetic theory of such states of aggregation is in accord with the known physical properties of matter in these states. The chemical properties of matter in so far as these determine chemical equilibrium, homogeneous or heterogeneous, can be correlated with our ideas of atomic structure. Indeed, it is on the basis of atomistics that the laws of chemical equilibrium were developed. The laws of reaction speed are likewise based upon the conception of atomic and molecular units. The atom in its modern development is in harmony with the known facts of electrolytic dissociation and of the equilibrium associated with such dissociation processes. The laws of surface chemistry, the domain of colloidal phenomena, are becoming the more understandable by the approach from the atomic and molecular viewpoint. The relationship between physical properties and molecular constitution, long known to be intimate, is yet more intelligible upon the basis of modern theories of atoms and molecules. In the domain of photochemistry there appear to be grounds for belief that therein lies a field where atomic behavior may be closely connected with the energy content which the body receives by radiation. The quantum theory of radiation may yet serve as the bridge connecting matter and energy in a more unified whole. It is not possible to elucidate all the relationships of material things by sole reference to material content. Side by side with the kinetic viewpoint the conclusions from the study of energy changes, the realm of energetics, must be placed. In the intelligent use of both, atomistics and energetics, progress will the more surely be achieved.

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[1] *J. Am. Chem Soc.*, **38**, 762 (1916)

[2] *Ann Physik*, **49**, 229 (1916).

[3] *J Am. Chem. Soc.*, **41**, 868, 1543 (1919), **42**, 274 (1920).

[4] Bohr, Nobel Prize Address, *Nature*, **112**, July 7 (1923).

CHAPTER II

THE ENERGETICS OF CHEMICAL CHANGE

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It is not possible completely to define any system by sole reference to the material content of the system, its atomic or molecular constituents. Associated with matter, independent of the fixed and unchangeable attributes of mass and form, are other properties which change with circumstances. Thus, for example, the temperature, pressure, heat content, motion, electrical potential, color may vary, without variation in the actual atomic or molecular content of the system. The properties of a copper rod when hot differ from those of a cold rod, those of a metal at high electrical potential from those of a metal uncharged. Motion and position convey definite properties to matter as can be illustrated by means of a rifle bullet or an avalanche. Even at a constant temperature the form of matter may vary. Gaseous, liquid and solid mercury either separate or coexistent are possible at a given temperature. The compression to which a given system is subjected may determine the changes which such a system will undergo. These variables, to which all forms of matter are subject and from which they cannot be entirely dissociated, are all energy variables of material things.

Every variation in the properties of a given species of matter is to be attributed to a variation of one or more of several energy variables. These energy variables are convertible one into the other, matter being the medium whereby such conversion is effected. Thus, heat energy is convertible into the energy of motion, the increased motion of the particles receiving such heat energy. Conversely, motion may be converted into heat energy by friction as was emphasized by Count Rumford in his inquiries concerning the heat resulting from the boring of cannon, or as demonstrated by Davy in the production of water by the friction of ice. Electrical energy can be expended in the production of heat energy or in the production of chemical change whereby chemical energy may be produced. Chemical energy is the source of most of our heat energy and is an instrument in the production of electrical energy. Many chemical actions are productive of light or may be made to produce it by way of other energy forms. This interchangeability of the forms of energy suggests therefore that energy, like mass, may be indestructible, but multiform or protean. Before, however, this concept of interconvertibility of energy can be examined in its quantitative aspects, the method of definition of energy must be examined in some detail.

The Definition of Energy: Every change in the condition of matter is to be ascribed to the operation of one or other forms of energy. The energy is composite of two factors, an intensity factor and a capacity factor, and is, indeed, the product of these two factors. The intensity factor is the measure of the resistance offered to the change of condition resulting from the operation of the energy. The energy can only operate when this resistance is either withdrawn or overcome. Such an intensity factor tending to produce a change is known as a force. A force, overcoming a resistance to an extent which we may designate as the capacity factor, performs work, expends energy. With a given force, the energy expended or the work performed varies directly as the capacity factor. In the production of motion the energy expended depends, therefore, on the force required to produce motion against the resistance and on the distance through which the object acted upon is moved. In the raising of an object of mass m against gravity, g, through a height h, the force exerted in opposition to gravity is mg and the capacity factor is the height h. The energy expended becomes, therefore, the product mgh. In the production of a volume change dv in any body against an external pressure p, the intensity factor or force, p, acts through a volume dv which is the capacity factor; the work done or energy expended is the product of the two factors, pdv. All energy changes of whatever form may be similarly resolved into two such factors.

The unit of energy in the c.g.s. system of units is the *erg*. It is the energy associated with a force of one *dyne* acting through one centimeter. A dyne is the force which, acting for one second on one gram, produces a velocity of one cm. per second in the body upon which the force is impressed. It is related to the action of gravity upon a mass. Gravity produces an acceleration of 980.6 cm. per sec. when acting upon a mass at sea-level and 45° latitude. The weight of one gram divided by $g = 980.6$ cm. per sec. is equivalent to one dyne. If the pressure of the atmosphere be defined as the pressure of 760 mm. of mercury under standard conditions, it may be expressed in dynes per sq. cm.

$$\begin{aligned}1 \text{ atmos.} &= 76 \times 13.59 = 1033.3 \text{ grams per sq. cm.}\\ &= 980.6 \times 1033.3 = 1013300 \text{ dynes per sq. cm.}\end{aligned}$$

THE FIRST LAW OF ENERGETICS

The Mechanical Equivalent of Heat: The first statement of the equivalence of heat and mechanical work is to be attributed to Mayer, 1842, who also attempted to ascertain the proportionality factor connecting the two energy quantities. Carnot (died 1832), in a posthumous publication, enunciated the same principle: "Heat is simply motive power or motion which has changed its form, for it is but a movement amongst the particles of a body. Whenever motive power is destroyed, an equivalent quantity of heat is produced; and, reciprocally, whenever heat is destroyed, motive power is developed." Mayer calculated the work involved in the expansion process when the specific heat of a gas is measured at constant pressure, this work, w, being then equated to the difference of the specific heats at constant pressure and constant volume, $c_p - c_v$ by the proportionality factor J, the mechanical equivalent of heat.

$$w = J(c_p - c_v).$$

The assumption involved in this calculation, namely, that heat energy and mechanical energy are equivalent, received its first experimental test by Joule, 1843-1880. He measured the heat produced q by most divergent mechanical processes and showed that in each case the proportionality factor, J, was approximately constant,

$$w = Jq.$$

Joule's experiments included the following:

(1) The heat produced when various liquids, water, oil and mercury, were stirred was compared with the work involved in producing the stirring by falling weights.

(2) The heat produced in a coil of wire by induction currents set up by rotation of the wire between the poles of an electromagnet was compared with the work done by falling weights in rotating the coil. The heat produced was measured by the rise in temperature of water in which the coil was rotated

(3) The heat produced by compression of water through narrow openings or capillaries was compared with the work required to drive the water through the openings or capillaries.

(4) The heat produced by compressing air to 22 atmospheres was compared with the work of compression.

(5) The heat produced by the passage of an electric current through a coil of wire immersed in a calorimetric fluid was compared with the energy of the current consumed.

Joule concluded that "772 lbs falling one foot would heat a pound of water one degree." Transformed into modern units Joule's measurements gave approximately

$$J = 4.17 \times 10^7 \text{ ergs per } 15° \text{ cal.}$$

The fact that independent methods of producing heat gave closely concordant values for J constituted the desired proof of the law of equivalence of heat energy and mechanical energy.

These early measurements have been repeated at intervals with greater refinements of technique. Rowland (1879), Miculescu (1892) and Reynolds and Moorby (1898) have determined J by the water-stirring method. Greater accuracy is achieved with the electric heating method, which has been employed by Griffiths (1893), Schuster and Gannon (1895), Callendar and Barnes (1902), Dieterici (1905). The former method gives a mean value

$$1\ (15°) \text{ cal.} = 4.1829 \times 10^7 \text{ ergs}^{1}$$

in good agreement with the determination of Miculescu, namely, 4.183×10^7 ergs.[1] By the electrical method the mean value is

$$1\ (15°) \text{ cal.} = 4.1809 \times 10^7 \text{ ergs}^{2}$$

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[1] A. W. Smith, *U. S. Weather Review*, **35**, 458 (1907).

[2] A. W. Smith, *Phys. Rev.*, **33**, 173 (1911).

when the electromotive force given by the Weston cell at 20° C. is defined by international agreement as 1.0183 volts. The average of these two determinations gives

$$1\,(15°)\text{ cal.} = 4.182 \times 10^7 \text{ ergs.}$$

Assuming that, with the new definition of electromotive force just mentioned, the volt-coulomb = 1 joule = 10^7 ergs, it follows that

$$1\,(15°)\text{ cal.} = 4.182\text{ joules; } 1\text{ joule} = 0.2423\text{ cal.}$$

Since a pressure of 1 atmosphere = 1013300 dynes per sq. cm.,

$$1\text{ cc.-atmos.} = 1013300\text{ ergs} = 0.10133\text{ joules.}$$

For a perfect gas, it will be shown that the fundamental equation connecting pressure, volume and temperature is, for one mol,

$$pv = RT,$$

where R is the gas constant. On the absolute temperature scale, 0° C = 273.1°. For one mol of gas under standard conditions the accepted value of v = 22412 cc. Hence,

$$R = \frac{22412 \times 1}{273} = 82.07\text{ cc. atmos. per degree.}$$

When transformed into the units of heat energy with the data already supplied

$$R = 1.9885\text{ calories per degree}$$

or

$$R = 8.316\text{ joules per degree.}$$

The Law of Conservation of Energy: This law, the first law of energetics, of which the equivalence of heat and mechanical energy is a special case, was definitely enunciated by Helmholz in a publication "Über die Erhaltung der Kraft,"[1] 1847. In this contribution, Helmholz demonstrated that the law of equivalence of heat and mechanical energy was a direct consequence of the century-old experience of investigators that it is impossible to produce a perpetual motion machine which, without expenditure of energy, shall produce energy. Definite proof of the impossibility of constructing such a machine cannot be achieved. It is necessary to rely upon the cumulative experience of investigators that the search for such a machine is fruitless. Furthermore, by assuming the impossibility of perpetual motion of this type, conclusions may be drawn which may be verified and, in their turn, be employed for the discovery of further facts or laws. Thus is attained the definite and general belief as to the truth of the fundamental law.

Helmholz pointed out that if the mechanical equivalent of heat were not an invariable quantity, it would be possible by suitable coupling of two processes of energy transformation, heat into mechanical work, to arrange that the heat produced in the stage of energy consumption should be more than sufficient to produce, in the second stage of the process, the same amount of energy as was consumed in the first stage. A perpetual motion machine would result. Heat energy would be continuously produced without the expenditure of any other energy form. The impossibility of such a perpetual motion machine compels our belief in the exact equivalence of heat and mechanical energy. Helmholz concluded therefore that: "In all processes occurring in an isolated system, the energy of the system remains constant."

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[1] *Ostwald's Klassiker*, No. 1.

The energy of a system is a function only of the state of the system at the given moment irrespective entirely of its past history, the manner or method of its origin. It is especially to be emphasized that this independence of past history refers only to systems whose identity is complete in all except the element of time. It is not enough that the atomic or molecular make-up shall be the same, for this may be secured even though the energies of the systems differ widely. Thus, for example, stick lead and electrolytic lead might be identical as to atomic content, pressure, temperature, volume and the like, but be different in energy content by reason of state of division, size of crystal and the like. Only in this wise can it follow that the energy change accompanying a transformation shall be a function only of the initial and final states of the system independent of the path between. For, if it were possible to effect a change in any system from state A to state B such that the energy change involved was dependent on the path by which the change was achieved, it would again be possible to construct a perpetual motion machine. All that would be necessary would be that one such method of conducting the change could be reversed. Then, by a suitable coupling of two processes,

$$A \rightarrow B \text{ by path I,}$$
$$B \rightarrow A \text{ by path II,}$$

if the energy produced in path I were larger than that consumed in path II, the system would be, on completion of the reverse process, in its initial state and a surplus of energy would be available. By repetition of the process, energy could be continuously produced—a perpetual motion would be possible. This is denied by human experience as embodied in the first law of energetics.

The Internal Energy of a System: The change from state A to state B of a given system is therefore accompanied by a perfectly definite energy increment which we may designate by ΔU and define by the expression

$$\Delta U = U_B - U_A.$$

In such case, U_B and U_A represent the energies of the system in states B and A respectively. They may be more definitely designated as the internal energies of the system in the two states. They are energy quantities of unknown absolute magnitude. They include the energy resultant from such factors as motion of the molecules, position of the molecules, molecular attraction, intra-molecular forces, intra-atomic vibrations, chemical and other unascertained forces. While, however, the absolute magnitude of such internal energy is not ascertainable, the change in such is definite and unchangeable for any given process of change.

Any such change in the internal energy of a system can only be achieved with a simultaneous change in the energy of surrounding systems, since the law of conservation of energy *must* be obeyed. An increment in internal energy of the system is secured, therefore, at the expense of a decrement in the energy of its surroundings. A decrement in the internal energy results in an increase of the energy of its surroundings. If we consider any process of change from state A to state B, whereby an increment of internal energy $\Delta U = U_B - U_A$ occurs, which results in the abstraction of heat, q, from the surroundings and simultaneously the performance of external work w by the system on the surroundings; then, by application of the law of conservation of energy,

$$\Delta U = q - w.$$

It has been shown that ΔU is a perfectly definite quantity for any given process, dependent only on the initial and final states, A and B. This is not true of either q or w. According as the experimental conditions change, q or w may both vary. Thus, if the process be carried out at constant volume and no other energy factors than those of mechanical energy are involved in the external work performed,

$$w = 0.$$

In such circumstances

$$\Delta U = q,$$

the whole increment of internal energy is secured at the expense of the heat of the surroundings. Ordinarily, processes are conducted, not at constant volume, but at constant pressure. In such case, a process will in general be accompanied by a volume change. The external work done by the system on the surroundings will be

$$p(v_B - v_A) = p.\Delta v,$$

p being the prevailing pressure, Δv the increase in volume of the system during the change from state A to state B. The heat q abstracted from the surroundings will be increased by an amount equal to the quantity $p\Delta v$, since

$$q = \Delta U + w = \Delta U + p\Delta v.$$

Conceivably the process may be conducted so that heat is neither gained nor lost by the system. Such a process is known as an *adiabatic* process. The quantity q is then zero. The work performed by the system on the surroundings must then be done at the expense of the internal energy of the system, or

$$\Delta U = -w.$$

It will later be shown that the quantity w may be composite of several forms of energy including mechanical, electrical, radiant energy and the like, and that, furthermore, the magnitude of such work performed may vary with the mode of conduct of the process.

It is thus evident that while U, the internal energy of the system, is a single-valued function of its several variables, pressure, temperature, volume and the like, dependent only on its state at the moment, this is not true concerning the quantities q and w. Whereas the small change of internal energy, dU, has the properties of a complete differential,

$$dU = \frac{\partial U}{\partial x}dx + \frac{\partial U}{\partial y}dy + \frac{\partial U}{\partial z}dz + \cdots,$$

where x, y, z, etc., are the several variables, the same is not true of the heat absorbed or external work performed by the system when such change in internal energy occurs. These may vary extremely, provided always that the law of energy conservation is satisfied,

$$\Delta U = q - w.$$

The quantities q and w are dependent *entirely* on the path by which the process is achieved.

The Heat Content of a System: Returning now to consideration of a process involving an increase in internal energy, heat absorption from the surroundings and a volume change v_A to v_B against a constant external pressure p. The first law of energetics demands that

$$\Delta U = U_B - U_A = q - p(v_B - v_A).$$

This may be transformed thus:

$$(U_B + pv_B) - (U_A + pv_A) = q.$$

In this case the heat, q, absorbed by the system is evidently defined by the initial and final states of the system. If we define a quantity

$$H = U + pv$$

and term this quantity, H, the heat content of the system, the equation becomes

$$H_B - H_A = q = \Delta H.$$

It will be noted that the quantity ΔH, like ΔU, is dependent only on the initial and final states of the system. The heat content of the system, H, like U, is a single-valued function of its several variables.

The Heat Capacity of a System: We may define the mean heat capacity, $\bar{c}$, of a system between two temperatures as the quantity of heat necessary to raise the system from the lower to the higher temperature divided by the temperature difference,

$$\bar{c}(T_2, T_1) = \frac{q}{T_2 - T_1}.$$

Since the heat capacity is known to vary with temperature, the true heat capacity at a given temperature may be defined by the differential expression

$$c = \frac{dq}{dT}.$$

The heat capacity may be determined either at constant volume or constant pressure, the magnitude of the heat capacity being dependent on the mode of experimentation. In the determination of heat capacity at constant volume, none of the absorbed heat is employed in the performance of external work. Hence, the heat absorbed, q, is equal to the increase in internal energy. We may, therefore, define heat capacity at constant volume per mol. of substance by the equation

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v.$$

At constant pressure, since

$$q = \Delta U + w,$$

the heat absorbed to produce a given rise of temperature will be greater by an amount equivalent to the external work performed by the system on the surroundings. Hence, we may define the mean heat capacity at constant pressure thus:

$$\bar{c}_p = \left(\frac{q}{T_2 - T_1}\right)_p = \left(\frac{\Delta U + p\Delta v}{T_2 - T_1}\right)_p = \left(\frac{\Delta H}{T_2 - T_1}\right)_p$$

and, for the true molecular heat capacity at constant pressure,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p.$$

The Heat of Chemical Reaction: Chemical reactions are in general accompanied by absorption of heat from or evolution of heat to the surroundings; they are either endothermic or exothermic. For a reaction occurring at constant volume, the heat absorbed or evolved is equal to the change in internal energy of the system, since no external work is performed. Hence $-\Delta U$ is a measure of the number of calories evolved in the reaction, or, in other words, a measure of the heat of reaction at constant volume. A thermochemical result of this type may be illustrated by the equation

$$CO + H_2O = CO_2 + H_2 + 10500 \text{ cals.}$$

Hence

$$\Delta U = -10500 \text{ cals.}$$

For reaction at constant pressure, p, accompanied by a volume increase, Δv, the heat absorbed, q, is equal to the increase in internal energy plus the external work performed,

$$q = \Delta U + p\Delta v = \Delta H.$$

At constant pressure, therefore, $-\Delta H$ is a measure of the calories produced in the given reaction,

$$C + O_2 = CO_2 + 97000 \text{ cals}; \ \Delta H = -97000 \text{ cals}.$$

The Constancy of the Heat of Reaction: Hess's Law: Since, in any process, both quantities ΔU and ΔH are dependent on the initial and final states of the system only and are independent of the path between, it follows that both the heat of reaction at constant volume and that at constant pressure, being numerically equal but opposite in sign to the increase in internal energy, ΔU, and that of heat content, ΔH, respectively, must also be defined by the initial and final states of the system independent of the path taken. In other words the heat evolved in any chemical reaction is independent of the manner in which the reaction is achieved whether in one or many steps. Thus, in the combustion of carbon to carbon dioxide the heat of reaction at constant pressure, $-\Delta H_1$, is equal to that for the two-stage process: (*a*) carbon to carbon monoxide, $-\Delta H_2$, (*b*) carbon monoxide to carbon dioxide, $-\Delta H_3$. Thus,

$$\begin{aligned} C + O_2 &= CO_2; & -\Delta H_1 &= 97000 \text{ cals.},\\ C + \tfrac{1}{2}O_2 &= CO; & -\Delta H_2 &= 29000 \text{ cals.},\\ CO + \tfrac{1}{2}O_2 &= CO_2; & -\Delta H_3 &= 68000 \text{ cals.},\end{aligned}$$

$$-\Delta H_1 = (-\Delta H_2) + (-\Delta H_3).$$

This consequence of the first law of energetics, which as will be shown later (Chapter VI) is of great utility in the science of thermochemistry, was first enunciated by Hess in 1840, prior to the formulation by Mayer and Joule of the law of conservation of energy, of which it is a special case. The law forms the theoretical basis of the classical experimental work of Thomsen and Berthelot on the thermal magnitudes of a wide variety of chemical compounds. For, the law of Hess involves as corollaries a number of useful conclusions. Thus, the heat of formation of a compound must be independent of the manner of its formation; the heat of reaction must be independent of the time consumed in the process; the heat of reaction must be equivalent to the sum of the heats of formation of the products of the reaction less the sum of the heats of formation of the initial reactants. The experimental methods of thermochemistry, the details of typical results obtained and of the methods of calculation will be given in a succeeding chapter (Chapter VI).

Heat of Reaction and Temperature: Kirchhoff's Law: The heat of reaction of a given process varies with the temperature, the mode of variation of which may be elucidated by consideration of a given process,

$$A \rightarrow B,$$

occurring at two temperatures T and $T + dT$ differing infinitesimally. For simplicity let the several processes be assumed to occur at constant volume. In the first place the reaction may be assumed to occur at temperature T whereby q calories of heat are yielded to the surroundings. The system B may now be raised from T to $T + dT$. This will require absorption of heat by the system equal to $C_v'.dT$, where C_v' is the heat capacity of the system B at constant volume in the given small temperature interval. In the second place, the process may be achieved by another path. The system A may be raised from T to $T + dT$ whereby analogously the heat absorbed will be $C_v.dT$. The reaction A to B may now be conducted at the temperature $T + dT$ whereby a heat evolution equal to $q + dq$ calories occurs. From the law of conservation of energy, the heat change from A at temperature T to B at temperature $T + dT$ is independent of the path by which it is achieved; otherwise, a perpetual motion machine could be realized. Hence, assigning positive values to heat absorbed by the system and negative values to heat given to the surroundings, we obtain by equating the two modes of procedure

$$- q + C_v'dT = C_v dT - (q + dq),$$

whence

$$dq = (C_v - C_v')dT$$

or

$$\frac{dq}{dT} = C_v - C_v'.$$

Since, at constant volume, q, the heat evolved in a process is equal to $- \Delta U$, we may write the equation

$$\frac{d(\Delta U)}{dT} = C_v' - C_v = \Delta C_v.$$

In a similar manner it may be shown that (see Chapter VI), operating at constant pressure instead of at constant volume,

$$\frac{d(\Delta H)}{dT} = \Delta C_p,$$

where ΔC_p represents the heat capacity of the products less that of the reactants. The temperature coefficient of the heat of reaction under any circumstances is therefore equal to the change in the heat capacity which the system undergoes in those circumstances. This law was first deduced by Kirchhoff[1] in 1858. It is applicable alike to chemical reactions and to all those processes such as fusion, vaporization and the like which we more usually term physical processes. More recently the applicability of the law in cases of sub-atomic nature has been demonstrated.

The Thomsen-Berthelot Principle: An Erroneous Concept of Chemical Affinity: The idea underlying the comprehensive investigations of Thomsen (1854 onwards) and of Berthelot in the domain of thermochemistry was the assumption that the heat of reaction was a direct measure of chemical affinity. In the words of Berthelot, "every chemical change which takes place without the aid of external energy tends to the production of that system which is accompanied by the development of the maximum amount of heat." This principle is wrong. Many reasons may be adduced to prove its incorrectness. If the principle were true, only exothermal reactions could take place unless external energy were simultaneously utilized. For, endothermic reactions would indicate a negative affinity or a repulsion. The existence of endothermic reactions had, therefore, to be explained by the proponents of the theory by assumption of the operation of secondary physical factors. Thus, the spontaneous solution of many salts in water, frequently endothermal, is apparently a contradiction of the Thomsen-Berthelot principle. It was "explained" that although the net observed heat effect was negative, the positive value, due to the affinity proper, was masked by secondary thermal magnitudes due to physical changes, e.g., the change of the solid salt to the fluid condition in solution. Such assumptions, impossible of test by measurement, only served to complicate what is, as will be shown, a very simple quantity, the chemical affinity of a system. The Thomsen-Berthelot principle implied, moreover, that reactions should proceed to completion in that direction in which exothermicity was developed. This had been definitely disproved by the researches of Berthollet at the beginning of the nineteenth century, the concept of balanced actions became indispensable when the Law of Mass Action was put forward by Guldberg and Waage in 1864. Balanced actions and equilibrium involve the simultaneous occurrence of exothermal and endothermal changes at one and the same temperature.

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[1] *Pogg. Ann.*, **103**, 454 (1858).

It will emerge in the subsequent discussion that the heat of reaction is not the true thermodynamic criterion for chemical reaction. On the contrary, the change of free energy, the capacity of the system to do chemical, electrical or mechanical work will be shown to be the correct measure of the driving force of a reaction. In certain special, but accidental, cases, the heat of reaction and the free energy of the process may be equal. In the majority of cases this will not be true. To demonstrate the correct relationship between these two magnitudes the first law of energetics is insufficient. New limitations on the convertibility of energy must first be discussed and these will lead to a second law of energetics. In the meantime it may be emphasized that the law of conservation of energy gives no information as to the *direction* of energy changes. It only insists that, whatever the direction of change, no energy shall be lost or gained by the system taken as a whole.

APPLICATIONS OF THE FIRST LAW TO GASES

The Internal Energy of an Ideal Gas: It will be shown subsequently that in general a gas may be defined by reference to two of the three variables, pressure, volume and temperature, any two of which will give the third a definite value. Since the internal energy of a substance is a function of its state at any given moment, it follows that the small change in internal energy dU of such a gas may be expressed by an equation of the form

$$dU = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial v} dv,$$

in which case v and T are chosen as the two variables. Now $\partial U/\partial T$ is the heat taken up by one mol. of gas when it is heated one degree without performing external work, for then

$$\Delta U = q.$$

This, however, is really the heat capacity at constant volume. Hence

$$\frac{\partial U}{\partial T} = C_v.$$

We may therefore write the above equation in the form

$$dU = C_v dT + \left(\frac{\partial U}{\partial v}\right) dv.$$

Hence, also, from the first law

$$q = C_v dT + \frac{\partial U}{\partial v} dv + w.$$

Now the work done in an expansion dv of a gas at constant pressure, p, $= pdv$. Hence

$$q = C_v dT + \frac{\partial U}{\partial v} dv + pdv.$$

If now the temperature change accompanying the expansion of a gas in a thermally insulated system (i.e., $q = 0$) against zero pressure (i.e., $pdv = 0$) be determined, such a temperature measurement will yield information relative to the change of internal energy with volume. This experiment was first carried out by Gay-Lussac and later by Joule, by allowing the gas from one vessel, I, to stream into an evacuated vessel, II, until pressure equilibrium was established in the complete system I + II. By having the system immersed in water in a calorimeter any temperature variation could be noted. The first experiments of this type led to the conclusion that dT was equal to zero. It was therefore concluded that, for such a system,

$$\frac{\partial U}{\partial v} = 0.$$

It follows, therefore, that for all such gaseous systems as would give this experimental result the internal energy would be independent of the volume, dependent only on the temperature of the system.

More accurate measurements, subsequently performed by Joule and Thomson (later Lord Kelvin), established the fact that this conclusion was incorrect for all real gases, but that it was approached the more closely the more the gas approached a condition of ideality. The lower the initial pressure in vessel I, or the higher the experimental temperature T, the more nearly did dT approach zero and therefore the more nearly did $\partial U/\partial v$ approach zero.

The real thermodynamic criterion to be fulfilled by any ideal gas may be learned by a study of the experimental method employed by Joule and Thomson to determine the temperature changes accompanying an expansion of a real gas. The change from a high pressure p_1 to a lower pressure p_2 was made to occur slowly by interposing a resistance to the gas flow. A porous plug divided the region of high pressure from that of low pressure. As the gas passed through the plug under compression on the high pressure side, p_1, the volume on the low pressure side was increased. Diagrammatically this may be illustrated in Fig. 1.

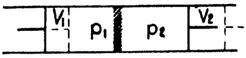

FIG. 1

The work done on the gas at high pressure p_1 for a gram mol. of the gas at volume v_1 compressed through the plug is obviously p_1v_1. On the low pressure side correspondingly the work done by the gas on the surroundings is p_2v_2. Now if Boyle's Law be obeyed by the gas in question,

$$p_1v_1 = p_2v_2,$$

it is evident that the system as a whole has performed no external work,

$$w = 0.$$

In a thermally insulated system q also is equal to zero. Under such circumstances

$$-C_v dT = \left(\frac{\partial U}{\partial v}\right) dv.$$

Whence, if $dT = 0$, it follows also that

$$\left(\frac{\partial U}{\partial v}\right)_T = 0.$$

Hence an ideal gas may be defined themodynamically as a gas fulfilling two conditions,

$$(a) \quad \left(\frac{\partial U}{\partial v}\right)_T = 0,$$

$$(b) \quad pv = \text{constant}.$$

Real Gases: The Joule-Thomson Coefficient: For real gases, in general, p_1v_1 will not be equal to p_2v_2. The external work performed by the system as a whole upon the surroundings will be

$$p_2v_2 - p_1v_1 = w.$$

According to the first law, for a process without heat absorption, a so-called *adiabatic* process,

$$\Delta U = U_2 - U_1 = -w = p_1v_1 - p_2v_2.$$

Hence

$$U_2 + p_2v_2 = U_1 + p_1v_1.$$

This equation may be transformed into

$$H_2 = H_1,$$

since

$$H = U + pv.$$

The free expansion of a real gas occurs, therefore, not with constant internal energy U but with constant heat content H. The Joule-Thomson coefficient is therefore definable as the change in temperature produced when the gas expands at unit pressure differential and constant heat content, or mathematically

$$k = \left(\frac{\partial T}{\partial p}\right)_H .$$

The Joule-Thomson coefficient for a number of gases under stated conditions is given in the following table.

TABLE I

JOULE-THOMSON COEFFICIENTS

		$k = \frac{T}{P}$ at Pressures				
Gas	$t°$ C.	0.6	2	10	15	40 atm.
Hydrogen	6.8	-0.030^a				
	90.1	-0.044^a				
Carbon Dioxide	0	1.35^a				1.46^c
	20	1.14^a	1.21^b	1.31^b	1.37^b	1.20^c
	40	0.96^a				1.04^c
	100	0.62^a				
		$P = 0$	25	50	100	150 Kg. cm.^{2}
Air[d]	-55	0.44	0.10	0.3	0.28	0.18
	0.6	0.27	0.25	0.24	0.19	0.16
	49	0.20	0.18	0.17	0.15	0.12
	150	0.09	0.09	0.07	0.06	0.05
	250	0.02	0.02	0.02	0.01	0.01
		$P = 1$	4.5	6.4 m. Hg		
Air[e]	0	0.399	0.378	0.359		
	50	0.298	0.278	0.270		
	100	0.224	0.210	0.213		

[a] Joule-Thomson.

[b] Natanson, *Wied. Ann.*, **31**, 502 (1887).

[c] Kester, *Phys. Rev.*, **21**, 260 (1905).

[d] Noell, *Forsch. Arbeiten* No. 184 (1916).

[e] Hoxton, *Phys. Rev.*, **13**, 438 (1919).

Now since in the free expansion of real gases, $H = U + pV$ is constant, i.e., $dH = d(U + pV) = 0$ and since H is also a single-valued function of any two of the variables, p, v, and T, that is,

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp,$$

it follows that, since $dH = 0$,

$$\frac{dT}{dp} = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{C_p}.$$

In other words the magnitude of the Joule-Thomson coefficient is determined by the variation in the quantity H with pressure at constant temperature since C_p is a definite numerical quantity.

The variation of H with pressure is determined by the respective variations of U and pv of which the quantity H is composed. For the majority of gases, with hydrogen and helium as exceptions, it has been experimentally determined that, with increasing pressure and at constant temperature, the product pv at first decreases and then increases. For moderate pressures, therefore, p_2v_2, the pressure-volume product on the low pressure side of the plug, will be greater than p_1v_1 for all gases excepting hydrogen and helium. Hence, in the porous plug experiment, the net external work done by the system upon the surroundings will be positive at moderate pressures for all gases except hydrogen and helium. In an adiabatic system cooling would therefore occur At higher pressures, when pv has increased sufficiently with increasing pressure, p_2v_2 will be less than p_1v_1 and the effect of Boyle's Law will be to cause a warming up of the system in passage through the plug

As far as the variation of U with pressure is concerned, with all real gases, the effect of expansion will be to produce a cooling of the gas. The molecular constituents of real gases exert an attractive force upon one another which is overcome when an expansion of the gas occurs. In every case therefore, under adiabatic conditions, the energy required in overcoming these attractive forces must come at the expense of the kinetic energy of the gas molecules and cooling will be produced.

The total observed effect will be composite of these two factors. They must operate in such manner that the heat content H shall be invariable throughout the process.

Rose-Innes has shown that the experimental measurements of Joule and Thomson could be represented by an equation of the type

$$\frac{dT}{dp} = \frac{a}{T} + b.$$

For air and carbon dioxide characteristic constants, a and b, were obtained, positive in sign. For hydrogen b was negative. In this last case evaluation of the constants $a = 64.1$, $b = -0.331$ indicated that at $T = 194°$ K. or $-79°$ C. the quantity dT/dp became zero. Below this temperature, the Joule-Thomson coefficient is positive, that is, cooling is produced in hydrogen below this temperature. This is in agreement with experimental investigations of Olzewski who showed that below 80° C. hydrogen could be cooled by expansion. All gases, other than hydrogen and helium, probably show inversion points at temperatures above ordinary room temperatures.

Joule and Thomson found that the Joule-Thomson coefficient varied inversely as the square of the absolute temperature

$$\frac{dT}{dP} = \frac{a}{T^2}.$$

This indicates that the lower the temperature, the greater the cooling effect produced per unit pressure gradient, a conclusion which has been experimentally verified in many cases.

The influence of pressure on the magnitude of the coefficient has been studied for oxygen at 0° C. over a considerable pressure range by Vogel.[1] The cooling effect decreased from 0.260° per atm. pressure gradient at 20 atm. pressure to 0.139° at 160 atm. pressure. Over a more limited pressure range Hoxton has studied the variation in the coefficient for air. He finds also a diminution of the coefficient with increasing pressure at constant temperature, the combined effects of pressure and temperature being representable by an empirical equation

$$k = -0.1975 + \frac{138}{T} - \frac{319P}{T^2}.$$

The Joule-Thomson effect is made use of practically for the liquefaction of gases by the so-called Linde-Hampson process. The gas cooled by expansion is utilized to pre-cool the compressed gas passing through the plug. A lower temperature is thereby produced in the gas upon expansion. The cooling is thus made cumulative until finally a temperature is attained at which liquefaction occurs. The efficiency of such a process may be calculated from the known data on the heat capacities of the gases at the two pressures, the Joule-Thomson coefficient, the boiling point and the heat of vaporization of the liquefied gas, when it is remembered that the heat content of the system undergoes no change.

The Relation between C_p and C_v: It has been shown that the quantities C_p and C_v are representable by the equations

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p,$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v.$$

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[1] München, 1910.

[2] *Phys. Rev.*, 13, 438 (1919).

Hence

$$C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v$$

$$= \left(\frac{\partial(U + pv)}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v$$

$$= \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v.$$

Now

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial v}\right)_T dv.$$

Hence

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p$$

or

$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v$$

$$= \left[p + \left(\frac{\partial U}{\partial v}\right)_T\right]\left(\frac{\partial v}{\partial T}\right)_p.$$

For an ideal gas it has been shown that

$$\left(\frac{\partial U}{\partial v}\right)_T = 0.$$

Hence, for such gases

$$C_p - C_v = p\left(\frac{\partial v}{\partial T}\right)_p.$$

Employing the equation of state for an ideal gas

$$pv = RT,$$

it follows that

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}.$$

Hence, for such gases

$$C_p - C_v = R.$$

Isothermal Expansion of an Ideal Gas: From the first law of energetics,

$$\Delta U = q - w,$$

it has been shown that ΔU is independent of volume change for an ideal gas. Hence, in the expansion of such a gas

$$q = w.$$

For an infinitesimal volume change dV at pressure p

$$q = pdV.$$

For a finite volume change, V_1 to V_2,

$$q = \int_{V_1}^{V_2} pdV.$$

Assuming for 1 mol. of gas that $pV = RT$, it follows that

$$q = \int_{V_1}^{V_2} RT\frac{dV}{V} = RTln\frac{V_2}{V_1}.$$

For an ideal gas we may also put $p_1V_1 = p_2V_2$, where p_1 and p_2 are the pressures concerned. The heat absorbed in the isothermal expansion becomes therefore

$$q = RTln\frac{p_1}{p_2}.$$

Adiabatic Expansion of an Ideal Gas: In this case, since the process is adiabatic,

$$q = 0.$$

Hence

$$\Delta U = -w = -p\Delta V.$$

Since external work is done by the system on the surroundings, the temperature of the gas must fall. The magnitude of the decrease in temperature may be calculated thus:

Since

$$\Delta U = C_v.\Delta T \qquad \text{and} \qquad pV = RT,$$

$$C_v.\Delta T = -p.\Delta V,$$

or, in the limit,

$$C_v.dT = -pdV,$$

whence on integration

$$C_v(T_1 - T_2) = \int_{V_1}^{V_2} pdV\cdot$$

Alternatively

$$C_v\frac{dT}{T} = -R\frac{dV}{V}$$

or

$$C_vdlnT = -RdlnV$$

or

$$C_vln\frac{T_2}{T_1} = Rln\frac{V_1}{V_2}.$$

Now, since $C_p - C_v = R$, and putting $C_p/C_v = \gamma$,

$$ln\frac{T_2}{T_1} = \frac{R}{C_v} ln\frac{V_1}{V_2},$$

$$ln\frac{T_2}{T_1} = (\gamma - 1) ln\frac{V_1}{V_2}$$

or

$$T_1V_1^{\gamma - 1} = T_2V_2^{\gamma - 1}.$$

Since $p_1V_1 = RT_1$ and $p_2V_2 = RT_2$, it follows that

$$p_1V_1^{\gamma} = p_2V_2^{\gamma}$$

or

$$p_1^{1-\gamma}T_1^{\gamma} = p_2^{1-\gamma}T_2^{\gamma}.$$

Cyclic Processes: A system which, upon completion of a change or series of changes, is in its original state is said to have completed a cycle. The whole process is known as a cyclic process. From the first law it follows that, since U is a single-valued function of its variables, dependent, therefore, only on the state of the system, independent of past history, for every cyclic process,

$$\Delta U = 0 = q - w.$$

If conducted at constant temperature the cycle is known as an isothermal cycle.

The cyclic process forms a useful method of studying the variation of matter when subjected to variations of energy content. The most celebrated of such cyclic processes is known as the Carnot Cycle.

The Carnot Cycle: This cycle comprises a four-stage process to which an ideal gas may be submitted. It was employed by Carnot to demonstrate the work available from a process of heat transfer. The cycle consists of four successive processes (*a*) an isothermal expansion, (*b*) an adiabatic expansion, (*c*) an isothermal compression at the lower temperature produced in the previous adiabatic expansion and (*d*) an adiabatic compression whereby the ideal gas is restored to its original temperature, pressure and volume. The accompanying diagram represents the *p-v* relationships in such a cycle starting at the state represented by *A* at temperature T_2, with the sequence of changes already detailed carrying the gas through states represented by the lines (*a*) *AB*, (*b*) *BC*, (*c*) *CD* and (*d*) *DA*.

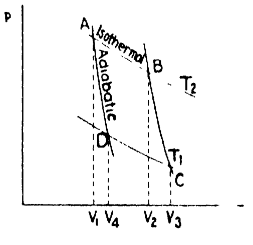

Fig. 2

The lines *AB* and *CD* represent the two isothermals, at the temperatures T_2 and T_1 ($T_2 > T_1$). The lines *BC* and *DA* represent the two adiabatics.

Let the respective p, v, T magnitudes be for A, p_1, V_1, T_2, for B, p_2, V_2, T_2, for C, p_3, v_3, T_1 and for D, p_4, V_4, T_1.

We may follow the changes occurring in the several stages thus:

Stage I. The gas expands isothermally from A to B at temperature T_2. Heat is absorbed equal in amount to the work done by the system on the surroundings, since, for an ideal gas, the change in internal energy is zero.

$$q_2 = w_1 = RT_2 ln \frac{V_2}{V_1} \cdot$$

Stage II. The gas expands adiabatically from B to C. The heat absorbed is zero; hence the work done is

$$w_2 = C_v(T_2 - T_1),$$

where $T_2 - T_1$ is the change in temperature resulting from the adiabatic expansion.

Stage III. The gas is compressed isothermally from C to D in a reservoir at T_1, whereby the heat q_1 is given up to the surroundings in amount equal to the work of compression

$$q_1 = w_3 = RT_1 ln \frac{V_3}{V_4} \cdot$$

Stage IV. The gas is compressed adiabatically from D to A. The work done on the gas is

$$w_4 = C_v(T_2 - T_1),$$

where $T_2 - T_1$ is the increase in temperature produced by the adiabatic compression.

The net heat absorbed by the gas in the whole cycle is, therefore,

$$q = q_2 - q_1 = RT_2 ln \frac{V_2}{V_1} - RT_1 ln \frac{V_3}{V_4} \cdot$$

From our knowledge of adiabatic expansions of an ideal gas we know that in the two adiabatic processes considered

$$C_v ln \frac{T_2}{T_1} = R ln \frac{V_3}{V_2} \quad \text{(Stage II)}$$

and

$$C_v ln \frac{T_2}{T_1} = R ln \frac{V_4}{V_1} \quad \text{(Stage IV)}.$$

Hence

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \quad \text{or} \quad \frac{V_2}{V_1} = \frac{V_3}{V_4} \cdot$$

Hence

$$q = q_2 - q_1 = R(T_2 - T_1) ln \frac{V_2}{V_1} \cdot$$

Similarly, the work done by the gas,

$$w = w_1 + w_2 - w_3 - w_4 = R(T_2 - T_1)ln\frac{V_2}{V_1},$$

which satisfies the condition for a cyclic process

$$w = q.$$

The work done may now be compared with the quantity of heat q_2 absorbed at the higher temperature T_2.

$$w = R(T_2 - T_1)ln\frac{V_2}{V_1},$$

$$q_2 = RT_2ln\frac{V_2}{V_1}.$$

Hence

$$w = q_2\frac{T_2 - T_1}{T_2}.$$

It is therefore evident that, in the cycle, a quantity of heat q_2 has been absorbed from the surroundings at a temperature T_2 and partly transformed into the work w, the remainder q_1 being given up to the surroundings when at a lower temperature T_1. The work obtained in such a process is a definite fraction, $(T_2 - T_1)/T_2$, of the absorbed heat. We may now proceed to an examination of the question whether this quantity of work w represents the maximum amount of work possible in such a heat transfer, whether also the same fraction would be obtainable were the system employed not an ideal gas. The answer to such problems leads us into the realm of the direction of energy change and the restrictions upon the interconvertibility of energy which experience has embodied in the second law of energetics.

The Second Law of Energetics

An inquiry into the direction of change which a given system will undergo may well be begun with an inquiry into some well-known examples of direction of change and the characteristics which such processes possess.

Reversible and Irreversible Processes: We are quite familiar with a variety of processes, both physical and chemical, which will proceed of themselves, or as we so designate them, spontaneously occurring processes. Heat is spontaneously transferred from a hot to a cold body either by contact or by radiation. Uniformity of temperature throughout the system will eventually result. With a concentrated solution in contact with a more dilute solution, diffusion of the solute will spontaneously occur and continue until a uniform concentration results. Gases permeate a vacuum. Similarly, the inter-diffusion of two gases when brought together is another familiar phenomenon. An electric current will flow along a conductor when differences of potential manifest themselves, just as water will flow from a region of higher level to a lower level until a uniform level is secured throughout the system. Many chemical reactions occur spontaneously; ammonia and hydrogen chloride gas at ordinary temperatures when brought into contact will react to yield solid ammonium chloride. All such processes proceed of themselves; *they are also, of themselves, irreversible.* All are tending to a state of greater stability. The *velocity* with which such a position of greater stability is approached may vary widely. The *trend* in that direction is definite and cannot be reversed by the system of itself. Only by the employment of external agencies can the direction of such processes be reversed. The final state which such a system attains is spoken of as a state of equilibrium. A system in such a state is characterized by the uniformity in the intensity of all its forms of energy. In reaching this finality many halting places may occur. The system in such case is in a state of metastable equilibrium. Thus, for example, hydrogen and oxygen at room temperatures are only apparently in equilibrium. In reality they are in partial or metastable equilibrium, as the introduction of a small amount of platinum black into the system would demonstrate. Water would result from the interaction of the gases. But, in no conceivable manner, without the intervention of external agencies, could the process be expected to reverse itself, to proceed from the water stage back to the state of the gas mixture. We might generalize such observations in the conclusion that: *spontaneously occurring processes are irreversible.*

Let us now examine the conditions under which we must operate in order to approximate to reversibility in the conduct of a process. The direction which any energy change takes is determined by the relative magnitudes of the intensity factors of the energy of the system and of its surroundings. At equilibrium the intensities of all the forms of energy are uniform. An infinitesimal variation in any one intensity factor will produce a change in that direction which will tend towards uniformity.

Imagine a pure liquid in equilibrium with its saturated vapor enclosed in a cylinder fitted with a piston the pressure upon which may be delicately adjusted. Let the apparatus be at constant temperature in a large reservoir from which the system may withdraw heat or to which it may give up heat. The piston will be stationary when the pressure on the piston is exactly equal to the pressure of the saturated vapor at the given temperature. Any displacement of the pressure on the piston, no matter how small, will cause a change to take place in the system, liquid-vapor. If the pressure on the piston be diminished infinitesimally, the piston will rise. The volume occupied by the saturated vapor will increase and hence a little of the liquid will evaporate to produce the saturation pressure. In doing this, heat will be abstracted from the reservoir. In this way, a process may be continuously operated, namely, the change from liquid to saturated vapor at a given temperature. The process will be exceedingly slow since the difference in the intensity factors is, under assumption, infinitesimally small. The process may also be reversed. Imagine a pressure on the piston infinitesimally greater than the saturated vapor pressure. The piston will, under such circumstances, compress the saturated vapor into a smaller volume, the supersaturation of the vapor which would thereby result being overcome by condensation of some of the vapor. By this reversal of the process vapor may be converted to liquid. Heat will be given up to the surrounding reservoir.

The energy expended in two such processes as we have just outlined may now be computed. Let the saturated vapor pressure at the constant temperature T be equal to p. In the first case let the pressure on the piston be $p - dp$, infinitesimally smaller than p. Let the volume change, dv, be infinitesimally small. The work expended by the system on the surroundings will be

$$(p - dp)dv = pdv - dp.dv.$$

If dp and dv are infinitesimally small, the second factor $dp.dv$ is an infinitesimal of the second order, negligible in comparison with $p.dv$. Substantially therefore, the work done is $p.dv$. In the second process considered, that of compression, the pressure on the piston must be slightly greater than p, say $p + dp$. Let the system, after the expansion, be compressed by such a pressure through a volume decrease $- dv$. The work done on the system will be

$$-(p + dp)dv = -(pdv + dp.dv)$$

or $- p.dv$ when second order infinitesimals are neglected. The system is now in its original condition, the heat changes paralleling the two processes having occurred and being demonstrably equal and opposite, provided that no accidental and irreversible processes have simultaneously occurred. For this, it is necessary to assume that the piston shall be both weightless and frictionless since otherwise irreversible changes, e.g., those due to friction, would doubtless have occurred. Such a process represents an ideal to which all naturally occurring processes may approximate without ever realizing. Such an ideal process, however, though not actually realizable, is, nevertheless, conceivable. From the mental conception and its consequences, definite conclusions may be reached. Such an ideal process is characterized by its complete reversibility in contrast to actual processes which will always contain elements of irreversibility to a greater or less degree. In the ideal process, all of the stages of the process may be repeated in inverse order in point of time, the net expenditure of energy by all the mechanical forces involved being zero on completion of the whole process.

One other example, involving another form of energy, may be cited to illustrate the concept of reversible processes and to show the approximation to the ideal process which may be achieved by a real process. The lead storage battery, when discharging, yields current at approximately 2 volts. When discharged the process may be reversed by supplying current to the battery. As normally operated, the process of discharge and charge is accompanied by a number of irreversible phenomena, diffusion of electrolyte, heat losses and the like. The discharge of the battery may, however, be secured under conditions approximating to the ideal reversible process by opposing to the flow of current from the battery a current at a potential infinitesimally smaller than that of the battery. Under such circumstances current would be drawn from the battery in infinitesimally small amounts at minute speed and the factors of irreversibility in the process would be reduced to a minimum. At any moment by increasing the opposing potential infinitesimally beyond that of the battery the direction of current flow would be reversed, the battery would begin to charge. Furthermore, as in the previous case the energy expenditure for any infinitesimal change in one direction will be exactly equal numerically to that expended in the reverse case. This type of reversible process is approximately obtained in the Poggendorf method of measurement of the electromotive forces of galvanic elements. The unknown potential is measured by opposing to it a potential of known magnitude, equality of potential being indicated by zero displacement of a galvanometer suitably placed in the electrical circuit. With such a system very minute quantities of current could be drawn from a galvanic element and the actual conditions of energy change would approximate very closely to the ideal reversible conditions.

Maximum Work: It is characteristic of such ideal reversible processes that the external work performed by the system undergoing change is the maximum amount of work that the system is capable of accomplishing It is very evident that, if all irreversible effects could be eliminated from a process, the efficiency of the process should be a maximum This is actually true. It may be made the more evident from a reconsideration of some ideal processes. In the isothermal expansion of an ideal gas through an infinitesimal volume change, dv, the work done is pdv. The magnitude of this quantity is obviously dependent on the opposing pressure p. When p is zero, expansion against a vacuum, the work done is zero. As p is increased the work done, pdv, also increases. The value attains a maximum when the driving pressure of the gas is infinitesimally greater than the opposing pressure. For, if these two pressures are equal, no volume change can occur; and if the opposing pressure be infinitesimally greater than the gas pressure, contraction in volume of the system will result. The maximum external work is therefore done when driving and opposing forces differ infinitesimally. This condition is, we have seen, that demanded by an ideal reversible process at all stages of its operation. The external work performed in a reversible process is therefore the maximum work available in the conduct of the process. In the expansion process just discussed, the maximum work, A, done by the system is therefore

$$A = pdv.$$

For a finite volume change conducted isothermally and reversibly

$$A = \int_{v_1}^{v_2} pdv,$$

which, as we have previously shown for an ideal gas, is

$$A = RTln\frac{v_2}{v_1} = RTln\frac{p_1}{p_2}\cdot$$

A little consideration will show also that the work done on the surroundings in an adiabatic expansion

$$C_v(T_1 - T_2) = \int_{v_1}^{v_2} p\,dv$$

also gives the maximum work available from the process. We may therefore conclude that in the complete cyclic process already considered, the Carnot Cycle, all the operations being conducted reversibly, the external work performed is the maximum work that can be accomplished in that cycle of operations. The relationship given by the Carnot Cycle may therefore be written

$$A = q_2 \frac{T_2 - T_1}{T_2},$$

the work done by the system in the transfer of heat q_2 from temperature T_2 to T_1 representing the maximum amount of work obtainable in an ideally conducted process. All real processes would yield a smaller amount of external work.

The maximum work which a given process is capable of accomplishing is a fixed and definite quantity characteristic of the process, determined solely by the initial and final states of the system independent of the path between. Were this not so it is immediately evident that a perpetual motion machine could be constructed whereby in the isothermal process

$$X \rightarrow Y$$

a path could be selected in which the maximum work A done by the system on the surroundings in passage from X to Y was numerically less than A', the maximum work done on the system in the reverse process Y to X. The system would then have completed an isothermal cycle and a quantity of work $A' - A$ would have resulted. The process could be repeated indefinitely. This, however, would be the perpetual motion machine denied by the First Law of Energetics. Hence it must follow that $A = A'$. Since these were any two possible methods of conducting the process, the maximum work must always be a constant quantity.[1]

As a corollary of this, it follows that the work done in an isothermal reversible cycle is equal to zero.

Furthermore, it may be shown that the fraction converted into useful work is independent of the mechanism whereby heat is transferred, provided that this mechanism is reversible. For, let us assume such a mechanism producing

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[1] The maximum work done is therefore analogous to ΔU, the change in internal energy of the system, in that it is a function of initial and final states, independent of the path between. The maximum work done by a process has therefore been defined by some authors in terms of two magnitudes, A_A and A_B, characteristic of the initial and final states A and B. Under such assumptions the maximum work which we have discussed is

$$A = A_A - A_B = -\Delta A.$$

an amount of work w' greater than w obtained in the Carnot Cycle previously considered. In such case a quantity of heat, q_2, will be taken from the reservoir at T_2 and a quantity of heat q_1' ($< q_1$) be given to the reservoir at T_1, whereby the relationship is obtained,

$$q_2 - q_1' = w'.$$

Then, by employing the Carnot Cycle for an ideal gas, in the reverse direction from that previously considered, a quantity of heat q_1 can be taken from the reservoir at T_1 and with the aid of a portion of the work w', actually the quantity w, an amount of heat q_2 can be put back into the reservoir at temperature T_2. As a result of this compound cycle the only change in the system as a whole is that a quantity of heat $q_1 - q_1'$ has been taken from a reservoir at T_1 and converted into useful work, $w' - w$, without causing any other permanent changes in the system as a whole. Experience teaches that such a machine is impossible. It is not in contradiction of the First Law of Energetics, since heat energy is consumed in the production of work. But the possibility of constructing such a machine is denied by the Second Law of Energetics, based upon the experience of man in the search for such a machine. Were such a machine possible, whereby heat could be continuously converted into work without compensation, an even more wonderful perpetual motion than that denied by the First Law would be possible. It would be possible continuously to utilize the large heat reservoirs of our environment to supply the motive power of our universe. It would be possible, for example, to drive a ship with the store of heat energy available in the ocean in which the ship was placed. Such a perpetual motion machine, which Ostwald has called a perpetual motion machine of the second kind, is specifically denied by experience and has resulted in the enunciation of the second law of energetics. For useful work to be produced from heat without compensation, a transfer of heat from a higher to a lower temperature is demanded. The fraction of heat converted into work is given by the equation

$$w = q_2 \frac{T_2 - T_1}{T_2}.$$

With an engine working in a heat reservoir at its own temperature it is obvious that $T_2 - T_1$ and hence w must be zero. It is therefore evident that whatever the reversible mechanism used for the heat transfer from a higher to a lower temperature reservoir the maximum work available is a constant.

Any reversible cycle can be shown to be equivalent to a sum of Carnot cycles. In the accompanying diagram, Fig. 3, let the continuous lines AB, BA represent the path of a reversible cycle. It is evident that the path A to B may

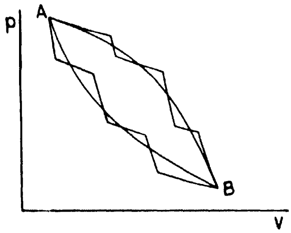

FIG. 3

be traversed by a number of isothermals and adiabatics as shown. Similarly the return path may be so traversed. The broken line path A to B approximates the more closely to the continuous curve AB the more minute the isothermal and adiabatic changes become. The same holds true for the reverse path BA. By prolonging the isothermals back into the enclosed portion of the diagram it is evident that the area ABA may be regarded as made up of a large number of infinitely small Carnot cycles actually equal to the reversible cycle under consideration. In the summation, all those portions of the small isothermals within the actual cycle will be traversed once in the one direction, once in the reverse direction so that the net resultant of such sections is zero. The properties of any reversible cycle will therefore be equal to the summation of the properties of all the Carnot cycles of which it may be regarded as composed.

The Concept of Entropy: In the discussion of the Carnot Cycle and in the generalization of the conclusions therefrom for any reversible cycle, we saw that the heat q_2 taken isothermally from a reservoir at T_2 was related to the heat q_1 given up to the reservoir at T_1 and to the maximum work A by means of the relation

$$q_2 - q_1 = w = A = \frac{T_2 - T_1}{T_2} q_2.$$

It follows, therefore, for any reversible cycle, that

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

or that

$$\frac{q_1}{T_1} = \frac{q_2}{T_2}.$$

If the cycle is not reversible, if any irreversible effects are present resulting in the dissipation of heat, it is evident that the work done, w, must be less than $[(T_2 - T_1)/T_2]\, q_2$. Under such circumstances

$$\frac{q_2 - q_1}{q_2} < \frac{T_2 - T_1}{T_2}$$

or

$$\frac{q_2}{T_2} < \frac{q_1}{T_1}.$$

Regarded from the standpoint of the machine conducting the Carnot Cycle the above expression for the equality of q_1/T_1 and of q_2/T_2 may be rearranged so that $+q$ represents heat absorbed by the machine. In such circumstance we have for the Carnot Cycle

$$\frac{(-q_1)}{T_1} = \frac{(q_2)}{T_2}$$

or

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0.$$

Similarly for an irreversible process

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} < 0,$$

where again q_1 and q_2 are the heats *absorbed by the machine* at the two temperatures.

For each individual Carnot Cycle into which a reversible cycle may be divided, the relationship

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$$

will hold. When the isothermal and adiabatic changes of each Carnot Cycle are infinitesimally small, the summation of the Carnot cycles is equal to the reversible cycle ABA in the preceding diagram. For the Carnot cycles we therefore have

$$\sum \frac{q}{T} = 0$$

and when the changes are infinitesimal we have correspondingly

$$\int \frac{dq}{T} = 0,$$

an expression which is therefore applicable to any reversible cycle irrespective of its nature or the path by which it is achieved provided that this be a reversible path. In the preceding figure, where the cycle is achieved in two stages A to B and B to A, it is evident that

$$\int \frac{dq}{T} = \int_A^B \frac{dq}{T} + \int_B^A \frac{dq}{T} = 0.$$

Both of these integrals are evidently independent of the path taken from A to B or conversely from B to A. Both are therefore determined by the properties of the initial and final states A and B. They are therefore evidently equal to the change in some single-valued function of the variables of the states A and B of the system. Let us express this by the relationship

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T},$$

whence it follows that

$$dS = \frac{dq}{T}.$$

These expressions give us a definition of the entropy of a system. The increase ΔS in the entropy, S, of a reversible process is the integral of all the heat changes which the system undergoes in passing from state A to state B, each heat change to be divided by the absolute temperature at which it occurred. The concept of entropy received this definition from Clausius who emphasized its importance in the formulation of the statement of the second law of energetics, its dependence on the state of the system and its independence of the path by which the state is achieved.

It may also be demonstrated that the entropy of an isolated system is the sum of the entropies of the component elements of the system Let us assume a system in which the component elements have internal energies respectively U_A, U_B, $U_C \cdots$, pressures p_A, p_B, $p_C \cdots$, volumes v_A, v_B, $v_C \cdots$ and entropies S_A, S_B, $S_C \cdots$, the whole system at a common temperature T. Let us assume for simplicity that external work changes in the system only involve mechanical energy. For any infinitesimal change occurring in the system, for example, to the component A, we have

$$dq_A = dU_A + p_A dv_A.$$

The corresponding entropy change will be

$$dS_A = \frac{dq_A}{T} = \frac{dU_A + pdv_A}{T}.$$

Similar equations hold for other changes in the system. Since the system is assumed isolated,

$$q_A + q_B + q_C + \cdots = 0$$

Hence

$$dS_A + dS_B + dS_C + \cdots = \frac{q_A + q_B + q_C + \cdots}{T} = 0.$$

Or alternatively,

$$d(S_A + S_B + S_C + \cdots) = 0$$

In other words, the entropy of an isolated system remains unchanged. Consequently the change of entropy in an adiabatic process is therefore zero. Also the entropy of the system is equal to the sum of the entropies of the component parts of the system.

Entropy Change in an Ideal Gas: For an ideal gas the heat absorbed in any process of change

$$q = \Delta U + p\Delta v.$$

For an infinitesimal change,

$$q = dU + pdv.$$

Hence

$$dS = \frac{q}{T} = \frac{dU + pdv}{T} = \frac{C_v dT + pdv}{T}.$$

If we assume that C_v is independent of temperature,

$$S = \int dS = C_v \int \frac{dT}{T} + R \int \frac{dv}{v} + \text{constant}$$
$$= C_v lnT + Rlnv + \text{constant}.$$

For a definite volume change, for example, an isothermal compression from v_A to v_B of one mol. of gas

$$S_B - S_A = Rln\frac{v_B}{v_A} \cdot$$

Since v_B is less than v_A, it is evident that the entropy of an ideal gas decreases during an isothermal compression. Conversely, in an isothermal expansion, the entropy of the gas increases by an amount equal to $Rln(v_B/v_A)$, where v_B is now greater than v_A.

Entropy Change in Irreversible Processes: The transfer of heat from a hotter to a colder system constitutes a simple irreversible process. Let us imagine an isolated system consisting of two reservoirs at temperatures T_2 and T_1 ($T_2 > T_1$) and a machine, e.g., an ideal gas, by which heat may be transferred. By allowing the gas to expand isothermally in the reservoir of heat at T_2, an amount of heat q may be taken from the reservoir. The gas may now be allowed to expand adiabatically until a temperature T_1 is attained. By placing the gas in contact with reservoir at T_1 and isothermally compressing, an amount of heat, q, may be communicated to the reservoir at T_1. The change in entropy of the gas is

$$\frac{q}{T_2} - \frac{q}{T_1} \cdot$$

The change in entropy of the reservoirs considered as a system is equal to

$$-\frac{q}{T_2} + \frac{q}{T_1} = \frac{q}{T_1} - \frac{q}{T_2} \cdot$$

Now, since T_2 is greater than T_1, we conclude that the conduction of heat from a reservoir of high temperature to one of low temperature results in an increase of entropy of the reservoir system.

The expansion of an ideal gas from volume v_A to volume v_B against a vacuum is another irreversible process, in which, as already shown,

$$S_B - S_A = Rln\frac{v_B}{v_A},$$

in which therefore an entropy increase of the gaseous system results.

We may therefore generalize our conclusions with regard to entropy change in the following manner. In irreversible processes, the entropy of all the systems involved in the change is increased. In ideal reversible processes, the entropy of the system as a whole is unchanged. The change in entropy of any portion of such a system undergoing a reversible change is equal to the heat which such portion of the system absorbs divided by the absolute temperature at which the heat is absorbed.

Now since all real processes are irreversible, we have a method of statement of the Second Law of Energetics. It may be thus expressed: *All naturally occurring processes are accompanied by an increase in the entropy of the system.* The content of the two laws of energetics may be summed up in the aphorism of Clausius: "The energy of the universe is constant; the entropy of the universe tends towards a maximum." This formulation of the second law provides us with one criterion of the direction of change which a given system will take if allowed to change spontaneously. The change will occur in that direction in which an increase in the entropy of the system is obtained.

Free Energy: We may now proceed to an examination of other thermodynamic magnitudes which have proved useful in the problems raised by the Second Law of Energetics, which will have, moreover, a greater applicability to problems of chemical change than the broader concept of entropy. Only at a later stage, when the theorem of Nernst, sometimes termed the Third Law of Thermodynamics, has received a detailed treatment, will the concept of entropy be applied in its most useful form.

For a reversible process we have seen that the entropy of an isolated system, machine plus surroundings, remains constant.

$$\Delta S = 0.$$

Let us define two quantities by the equations

$$A = U - TS$$

and

$$F = H - TS = (U + pv) - TS = A + pv.$$

For any given isothermal change we can derive corresponding equations as, for example,

$$\Delta A = \Delta U - T\Delta S.$$

If this equation apply to any reversible change at temperature T, it follows from the preceding section that $T\Delta S$ is equal to q, the heat absorbed in the process. Hence, from the equation for the first law,

$$\Delta U = q - w,$$

it follows that

$$\Delta A = -w$$

or alternatively that $-\Delta A$ is equal to the total work done by the system on the surroundings and, since the process in question is assumed to be reversible, it represents the maximum work which the system is capable of accomplishing. It is, in other words, identical with the quantity which we have designated by the term A in the earlier sections.

In a process at constant temperature and constant pressure it is obvious that the work done by the system will be composite of two factors, that involved in the volume change, namely, $p\Delta v$ and a residual quantity w' which may be one of many energy quantities. A frequent form of such energy obtained in the conduct of chemical processes is electrical energy. Radiant energy, in the form of light, may be produced. Similarly, other forms are possible. In such case $w' + p\Delta v = w$. The quantity $p.\Delta v$ is constant irrespective of the mode of conduct of the process. The magnitude of the quantity w' will vary with the mode of conduct of the process. The greater the degree of irreversibility in the process, the less will w' be. It is conceivable that it may be zero, indicating complete irreversibility. The more the process approximates to reversible conditions, that is, the more w approximates to its maximum value, the greater will w' become. With a completely reversible isothermal process at constant pressure

$$w' + p\Delta v = w = -\Delta A.$$

Hence

$$w' = -\Delta A - p\Delta v.$$

Whence, from the equation $F = H - TS = A + pv$,

$$w' = -\Delta F = F_A - F_B.$$

These two quantities $-\Delta A$, the "Free Energy" of Helmholz, and $-\Delta F$, the "Thermodynamic Potential" of Gibbs, are, as will be shown, of extraordinary utility in dealing with processes of chemical change. It is apparent that the quantity $-\Delta A$ is of importance when the variables chosen are volume and temperature. For pressure and temperature as chief variables the quantity ΔF has the preference; this will be generally true since constant temperature or constant pressure normally prevail in most chemical experiments. For reaction at constant volume and pressure it is evident that

$$\Delta A = \Delta F.$$

From the equation

$$F = H - TS$$

we obtain by differentiation with respect to pressure

$$\left(\frac{\partial F}{\partial p}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T - T\left(\frac{\partial S}{\partial p}\right)_T.$$

Now

$$H = U + pv$$

or

$$dH = dU + pdv + vdp = TdS + vdp.$$

Hence

$$v = \left(\frac{\partial H}{\partial p}\right)_T - T\left(\frac{\partial S}{\partial p}\right)_T.$$

Hence also

$$\left(\frac{\partial F}{\partial p}\right)_T = v.$$

Or, for an isothermal process,

$$\int dF = \int v dp.$$

Similarly, the variation of F with temperature may be ascertained. Thus,

$$F = H - TS.$$

Hence

$$\left(\frac{\partial F}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_p - S.$$

Now

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p \quad \text{and} \quad T\left(\frac{\partial S}{\partial T}\right)_p = C_p.$$

Hence

$$\left(\frac{\partial F}{\partial T}\right)_p = -S = \frac{F - H}{T},$$

or

$$F - H = T\left(\frac{\partial F}{\partial T}\right)_p.$$

Correspondingly for a change in the quantity F in an isothermal process of change from state A to state B we may write this equation in the form

$$\left(\frac{\partial(\Delta F)}{\partial T}\right)_p = \frac{\Delta F - \Delta H}{T}$$

or

$$\Delta F - \Delta H = T\left(\frac{\partial(\Delta F)}{\partial T}\right)_p.$$

This equation enables us to calculate the change in thermodynamic potential of a reaction at any temperature when it is known at any given temperature. For a reaction at constant volume the corresponding equation will be

$$\Delta A - \Delta U = T\left(\frac{\partial(\Delta A)}{\partial T}\right)_v.$$

Applied to reversible galvanic cells these equations give us the well-known Gibbs-Helmholz equation. For a reversible cell having an electromotive force E at constant temperature T and a temperature coefficient dE/dT it is evident that, when operated at constant pressure p,

$$-\Delta F = nFE,$$

where nF is the number of coulombs of electricity yielded by the cell when operated under such circumstances that the maximum electrical work is accomplished. Hence therefore,

$$-nFE - \Delta H = -nFT\frac{dE}{dT}$$

or

$$nFE + \Delta H = nFT\frac{dE}{dT}.$$

Thermodynamic Equilibrium: A condition of equilibrium may be defined by stating that a system is in equilibrium when it shows no change of state in any particular with time. The system must be in a state of absolute rest. A state of partial equilibrium is familiar to every one. A mixture of hydrogen and oxygen at room temperatures is one such example already discussed in an earlier section.

A state of absolute rest is difficult to determine experimentally. This fact may be illustrated by the case of the mixture of hydrogen and oxygen just cited. If, for example, such a gas mixture were stored over mercury at room temperature, no change in volume would be noted over long periods of time. This does not mean, however, that no chemical change is occurring. Let it be assumed that 10^6 molecules of hydrogen and half this number of oxygen molecules are reacting *per second*. A simple calculation, employing for the Avogadro number, $N = 6.06 \times 10^{23}$ moleculus per gram molecule, will reveal that it would require a period of observation extending over 6×10^7 years before a volume contraction of 1 cc. could be observed. It is very evident, therefore, that any thermodynamic criteria for a state of absolute rest or of chemical equilibrium would be extremely valuable if not absolutely necessary.

We saw that it was characteristic of reversible processes that the smallest change in any of the intensity factors of the various energy quantities obtaining in the system was sufficient to cause a displacement of the system in one or other direction dependent on the sign of the change in the intensity factor. The same is true for any system in thermal equilibrium. Every infinitesimal change in such a system is reversible. We have seen that the criterion of this reversibility is that

$$dS = 0.$$

Now

$$F = H - TS$$

or

$$= U + pv - TS.$$

Hence, by differentiation,

$$dF = dU - TdS - SdT + pdv + vdp.$$

For reversible processes

$$dU - TdS = -pdv.$$

Hence

$$dF = -SdT + vdp.$$

It therefore follows that, for reversible changes at constant temperature and constant pressure,

$$dF = 0.$$

This expression becomes, therefore, a second criterion for equilibrium conditions. A system is in equilibrium when a small displacement in the conditions of the system can be accomplished without change in the thermodynamic potential.

For a system which is not in equilibrium the direction of change may also be stated. Any naturally occurring process results in an increase in the entropy of the system as a whole. Now, since

$$\Delta F = \Delta H - T\Delta S,$$

it is evident that $T\Delta S$ must always be positive in spontaneously occurring processes. If the system be isolated, it is clear that ΔH is zero. Hence ΔF must be negative in all such processes. We therefore conclude that the thermodynamic potential of all spontaneously occurring processes decreases. It will be shown in the sequel how important is this criterion of the direction of chemical change

Some writers have assigned to this concept of thermodynamic potential the term "free energy" originally used by Helmholz to designate the function A which we have considered above. It is evident that the thermodynamic potential is in reality the free energy change accompanying an isobaric process. In succeeding chapters the term free energy is used to denote F, in agreement with recent practice among physical chemists in America.

The magnitude of the free energy decrease accompanying a process is evidently a measure of the tendency of a system to react—a concept which from very earliest times has been designated as the chemical affinity of a system. The free energy decrease gives therefore a quantitative measure of the tendency of the system to undergo reaction. It is immediately evident that the information we possess concerning the magnitude of the free energy decrease is in accord with our ideas concerning affinity. If a system is in equilibrium, the chemical affinity is nil. This is in accord with our deduction that for systems in equilibrium $dF = 0$. The further removed a system is from its equilibrium state the greater the chemical affinity. Likewise the greater is the free energy decrease accompanying the change of such a system to equilibrium conditions.

In the succeeding chapters of the book, the many applications of the fundamental concepts herein detailed will be brought forward. It will emerge that the thermodynamic method constitutes a most effective auxiliary of the atomistic or kinetic method of treatment, the one confirming and in some cases amplifying the conclusions deduced by the aid of the other.

CHAPTER III

THE GASEOUS STATE OF AGGREGATION

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The gaseous state may be defined as that homogeneous state which matter assumes when any given amount of it fills completely an otherwise void system of any volume. The behavior of matter in this state may be most readily understood from the standpoint of the kinetic theory. The validity of this theory rests upon two fundamental postulates the Daltonian concept of matter and the hypothesis that the motion of the particles embodied in this concept manifests itself by the phenomenon of temperature. The first has become almost axiomatic in the realm of physical science and the second has had almost direct proof from the study of the Brownian movement and of the radiometer. The fact that every experimental test of the theory has borne out its predictions except in cases where, for the sake of simplicity, the derivations are approximate or where experimental observations are inaccurate constitutes real evidence for its validity The development of this remarkable generalization may be attributed chiefly to the work of Avogadro, Clausius, Maxwell, Boltzmann, van der Waals and Jeans The contributions of these men have become so familiar that rarely are their names associated with particular phases, in but few sections that follow could the names of one or more of these men not be associated with the fundamental theoretical contribution.

The Ideal Gas Laws: The experiments carried out by Boyle[1] and Gay-Lussac[2] on the relationship between the volume, pressure, and temperature of a gas was expressed by these investigators in the form of the following empirical rules:

At constant temperature,

$$p_1v_1 = p_0v_0, \tag{1}$$

At constant volume,

$$p_1 = p_0\left(1 + \frac{t}{273}\right). \tag{2}$$

At constant pressure,

$$v_1 = v_0\left(1 + \frac{t}{273}\right), \tag{3}$$

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[1] Boyle, Paper read before the Royal Society, 1661.

[2] Gay-Lussac, *Ann. Chim. Phys.*, **43**, 137 (1802).

where p_0 and v_0 are the pressure and volume respectively of a given mass of gas at zero degrees Centigrade; t is the temperature in degrees Centigrade; p_1 and v_1 are the pressure and volume respectively under the changed conditions. These three equations may be replaced by a single one, when volume, pressure, and temperature vary simultaneously:

$$p_1v_1 = p_0v_0\left(1 + \frac{t}{273}\right) = kT, \tag{4}$$

in which k is a constant equal to $\frac{p_0v_0}{273}$ and T is equal to $t + 273$, i.e., the absolute temperature. This equation was first deduced from experimental facts, and, at the time of its deduction, had no theoretical significance. The generality of the above equation was not overlooked and suppositions were readily forthcoming in order that its form might be explained. The result was the beginning of the kinetic theory.

The Kinetic Theory: Among the first to suggest the explanation for the behavior of gases was Daniel Bernouilli.[1] The fundamental assumptions may be stated briefly as follows. A gas is composed of discrete particles (molecules), which have the form of spheres and which are perfectly elastic. These are in continual and chaotic motion and obey Newton's laws. In virtue of this motion, the gas has a certain amount of intrinsic energy, and since it is energy in its most degraded form, it manifests itself in the form of heat. This energy is composite of two factors—one, an intensity factor, viz., temperature, and the other, a capacity factor, or entropy. Qualitatively, this hypothesis explains the experimental facts. The pressure on the walls of the containing vessel is due to the force of the impacts of the molecules. Compressing the gas increases the number of molecules per unit volume, and hence the number of impacts per second upon the walls of the containing vessel, i.e., the pressure increases. Raising the temperature of a gas at constant volume increases the average velocity of the molecules, and hence the force with which they strike the walls, i.e., the pressure is increased.

The above hypothesis also permits of a quantitative treatment. Consider a mass of gas in the steady state enclosed in a cube of length L. In order to calculate the pressure, let it be assumed that the molecules, which are in reality moving with velocities varying from zero to infinity, are all moving with the same velocity, u, which is the square root of the mean square velocity.[2] This velocity is resolvable into components normal to the three directions, related to u in the following way:

$$u_x^2 + u_y^2 + u_z^2 = u^2. \tag{5}$$

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[1] Bernouilli, Hydrodynamica (1738).

[2] The square root of the mean square velocity, u, is related to the average velocity, u_a, in the following way:

$$u_a = \sqrt{\frac{8u}{3\pi}} = 0.92u.$$

Pressure is a force, and, from Newton's second law, is equal to the product of the mass, m, of a particle and its acceleration, a.

$$f = ma = m\frac{du}{dt} = \frac{d(mu)}{dt}\,. \tag{6}$$

A molecule with component of velocity, x, in the direction normal to the side upon which it impinges, approaches this side with momentum $+ mu_x$; after impact it rebounds with a momentum $- mu_x$, the change in momentum being $2mu_x$. The number of impacts in one direction per unit of time is $\frac{u_x}{L}$, and the total change in momentum in one direction per unit of time is $\frac{2mu_x^2}{L}$; the total change in momentum per unit of time in all three directions is

$$\frac{2mu_x^2}{L} + \frac{2mu_y^2}{L} + \frac{2mu_z^2}{L},$$

which expression, by equation (5), is equal to $\frac{2mu^2}{L}\cdot$ Since the total area upon which the pressure is exerted is $6L^2$, the pressure per unit area is $\frac{1}{3}\frac{mu^2}{L^3}$, or $\frac{1}{3}\frac{mu^2}{V}$, where V is the volume of the cube. If, instead of one molecule in the cube, there are n, the expression for the pressure becomes

$$p = \frac{1}{3}\frac{mnu^2}{V}$$

or

$$pV = \tfrac{1}{3}mnu^2, \tag{7}$$

and, since the kinetic energy of the molecules is equal to $\frac{1}{2}mnu^2$,

$$pV = \tfrac{2}{3}E, \tag{8}$$

where E is the kinetic energy of the molecules. The kinetic energy of the molecules, by one of the fundamental assumptions, is a measure of their heat energy, and, since this energy is proportional to the absolute temperature,

$$pV \propto T$$

or

$$pV = RT, \tag{9}$$

in which R is a universal constant and identifiable with k in equation (4). The fundamental equation found by experiment is thus derived from the postulates of the kinetic theory.

Experiments have shown that no real gases obey equation (4) exactly. It is therefore important to examine the fundamental assumptions to see wherein unjustified simplifying conditions have been introduced. Firstly, no account was taken of the attractive forces between the molecules; such an attraction would result in decreasing the velocities of the molecules in the marginal regions of the gas, and therefore the real pressure is greater than that measured. Secondly, if the molecules themselves have a definite volume, the number of impacts of any one molecule would be $\frac{u_x}{L - d}$, where d is the diameter of the molecule, instead of $\frac{u_x}{L}$ as assumed in the preceding derivation. Thirdly, the molecules were assumed to be perfect spheres; if they are not, the change in momentum after an impact on the wall is not necessarily $2mu$, since part of the energy of translation may have been changed into rotational energy. Equations taking into account these corrections have been put forward by many investigators, the most important of which equations is due to van der Waals. His equation will be taken up in considerable detail later.

A gas obeying equation (9) exactly is commonly termed an ideal gas. All gases approximate more and more nearly to the state of ideality as the pressure is decreased and as the temperature is increased. The concept of an ideal gas is often extremely useful and will be used repeatedly.

Avogadro's Hypothesis: Equation (9) is valid for a given mass of a particular gas. If the mass of gas taken as a standard is the molecular weight expressed in grams, the constant R assumes a definite value, and the general equation for any mass of any ideal gas is

$$pv = \frac{m}{M} RT,$$

where m is the mass of the gas considered and M its molecular weight. The experiments which led to the above generalization are also the experiments that led to Avogadro's hypothesis;[1] in fact, this hypothesis is embodied in the above equation. Two gases are at the same temperature when the mean kinetic energies of their molecules are equal,

$$\tfrac{1}{2} m_1 u_1^2 = \tfrac{1}{2} m_2 u_2^2.$$

They exert the same pressure when their kinetic energies per unit volume are equal (equation 7),

$$\tfrac{2}{3}(\tfrac{1}{2} N_1 m_1 u_1^2) = \tfrac{2}{3}(\tfrac{1}{2} N_2 m_2 u_2^2)$$

or

$$\rho_1 u_1^2 = \rho_2 u_2^2,$$

where ρ_1 and ρ_2 are the densities of the gases. From these equations it follows that, if two gases are under the same conditions of temperature and pressure, their densities must be in the same ratio as their molecular weights, or

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[1] Avogadro, J. de Physique par Delametherie 73, 58 (1811).

$$\rho_1 : \rho_2 = m_1 : m_2. \qquad (10)$$

The density of a gas is by definition equal to the molecular mass times the number of molecules per unit volume, i.e., $\rho_1 = N_1m_1$ and $\rho_2 = N_2m_2$; hence,

$$N_1m_1 : N_2m_2 = m_1 : m_2$$

or

$$N_1 = N_2.$$

This equation expresses the very important generalization of Avogadro, that, in equal volumes of gases under the same conditions of temperature and pressure, there are the same number of molecules.

The facts embodied in the above equations are in agreement with the observations of Gay-Lussac and Humboldt that the reacting volumes of gaseous substances at the same temperature and pressure are in the ratio of small whole numbers. According to one of Dalton's fundamental assumptions, chemical reactions take place only between whole numbers of atoms, from which the following expression is obtained,

$$m_1 : m_2 = n_1Q_1 : n_2Q_2,$$

where n_1 and n_2 are integers and Q_1 and Q_2 are stoichiometrical weights of the two gases. From equation (10),

$$\rho_1 : \rho_2 = m_1 : m_2 = n_1Q_1 : n_2Q_2.$$

The densities of the two gases are equal, respectively, to $\frac{Q_1}{V_1}$ and $\frac{Q_2}{V_2}$, where V_1 and V_2 are the reacting volumes. Hence,

$$\frac{Q_1}{V_1} : \frac{Q_2}{V_2} = n_1Q_1 : n_2Q_2$$

or

$$V_1 : V_2 = n_2 : n_1.$$

This equation expresses mathematically the observation of Gay-Lussac in connection with volume relationships of gaseous reactants.

Adiabatic Expansions: In Chapter II it was learned that the internal energy of an ideal gas at constant temperature is independent of its volume, i.e., $\left(\frac{\partial \Delta U}{\partial V}\right)_T = 0$. In the same chapter it was also learned that $\Delta U = q - w$, where w is the work done by the system and q is the heat absorbed from the surroundings. Since ΔU is zero during the isothermal expansion of a perfect gas, $w = q$, or the work done by the system is equal to the heat absorbed. Consider an ideal gas expanding in a thermally insulated vessel ($q = 0$). Two cases are to be considered, one in which the gas performs work by expanding against an external pressure and another in which it expands against zero pressure, and therefore does no work. The first case is realizable in a mechanism as illustrated in Fig. 1, case I. Under these conditions, the gas at pressure p_1 expands by driving the piston P from position x_1 to position x_2. In this case the gas does work in amount equal to or less than $Rln\,\frac{v_1}{v_2}$ (the inequality or equality being valid, depending upon the reversibility of the expansion). Since q is equal to zero, this work must be performed at the expense of the internal energy of the gas, i.e., the gas cools. In case II, where the gas expands upon puncturing the diaphragm D, no work is done, and the temperature of the gas remains constant.

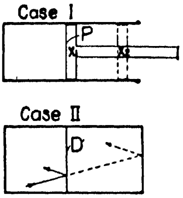

FIG. 1

The different processes may be visualized in terms of the kinetic theory as follows. In case I, when a molecule strikes the piston, which is moving (it matters not how slowly), it will rebound with a lower velocity than it impinges, since its motion has been effective in driving back the piston. This diminution in velocity of the molecules striking the piston means a diminished kinetic energy, and therefore a lowering of the temperature of the gas. If the piston had been suddenly moved to its final position with a velocity greater than that of any of the impinging molecules, no diminution of the velocity of the molecules would have occurred, and there would have been no cooling effect. In reality, this is exactly what happens in case II. When the diaphragm is suddenly punctured, the gas molecules pass through unaltered as regards their velocities, and, therefore, there is no cooling effect.

The pressure-volume relationship during an adiabatic expansion may be obtained in the following way. In Fig. 2, AB is an adiabatic curve, obtained when pressure is plotted against volume. The change x-to-y may be thought of as carried out in two infinitesimally small steps, one at constant volume and the other at constant pressure. If C_p is the specific heat of the gas at constant pressure and C_v its specific heat at constant volume, the total heat effect is

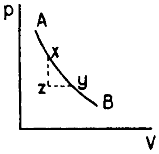

FIG. 2

$$C_p(\partial T)_p + C_v(\partial T)_v.$$

Since the change is an adiabatic one, this sum is equal to zero. Employment of the equation $pv = RT$ gives, by differentiation of temperature first with respect to volume (at constant pressure) and then with respect to pressure (at constant volume), the following expressions:

$$\left(\frac{\partial T}{\partial v}\right)_p = \frac{p}{R}; \quad \left(\frac{\partial T}{\partial p}\right)_v = \frac{v}{R},$$

$$C_p \cdot \frac{p}{R} \cdot \partial v + C_v \cdot \frac{v}{R} \cdot \partial p = 0.$$

If $\frac{C_p}{C_v}$ is replaced by γ and p and v by their equals $\frac{RT}{v}$ and $\frac{RT}{p}$, respectively, the following equation is obtained:

$$\gamma \frac{\partial v}{v} + \frac{\partial p}{p} = 0$$

or, integrated,

$$\gamma \log v + \log p = \text{constant}, \qquad (11)$$
$$pv^\gamma = \text{constant},$$

or, in an alternative form,

$$Tv^{\gamma-1} = \text{constant}.$$

The maximum work obtainable from an adiabatic expansion may be calculated in the following way:

$$A = \int_{v_1}^{v_2} p dv = \int_{v_1}^{v_2} k \frac{dv}{v^\gamma} = \int_{v_1}^{v_2} k v^{-\gamma} dv,$$

where $k = pv^\gamma$ or, integrated,

$$A = \frac{p_2v_2 - p_1v_1}{1 - \gamma}. \qquad (12)$$

Diffusion Through Capillary Tubes: The phenomenon of gaseous diffusion can be strikingly visualized with the aid of the kinetic theory. Let A (Fig. 3) be a vessel containing an equimolecular mixture of oxygen and hydrogen, connected by capillary tubes to the vessel B in which a vacuum is maintained. Provided the diameters of the capillary tubes are much smaller than the average distance between molecules, it is found that four times as much hydrogen diffuses through the tubes as oxygen. Only those molecules which strike the openings of the tube will diffuse. Although there is the same number of each kind of molecule, the hydrogen molecules are moving with much greater velocities, and therefore more of them will strike the openings per unit of time than oxygen molecules. From equation (7), the velocities of the two types of molecules are given by

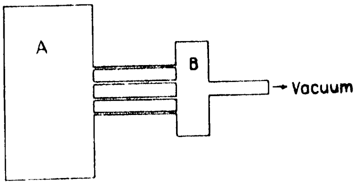

Fig. 3

$$U_{O_2} = \sqrt{\frac{3pv}{m_{O_2}n}} = \sqrt{\frac{3RT}{m_{O_2}n}}$$

and

$$U_{H_2} = \sqrt{\frac{3pv}{m_{H_2}n}} = \sqrt{\frac{3RT}{m_{H_2}n}}.$$

Since n is the same in the two cases,

$$\frac{U_{H_2}}{U_{O_2}} = \sqrt{\frac{32}{2}} = 4. \tag{13}$$

This means that hydrogen has four times the chance of diffusion that oxygen has, and therefore its accumulation in the evacuated vessel should be four times that of the oxygen. Evidence confirming this deduction was presented by Graham[1] from his experiments dealing with the diffusion of gases through porous plates.

In the above experiment, the unequal rates of diffusion of the two gases causes the mixture in A to become relatively richer in oxygen. As before, vessel A is filled with a mixture of hydrogen and oxygen, each initially at a partial pressure of one half atmosphere. The vessel B is connected with an exhaust pump. The number of oxygen molecules which strike the openings of the capillaries in time dt is equal to $K \frac{1}{\sqrt{M_{O_2}}} N dt$, where K is a constant depending on the dimensions of the apparatus, N is the number of oxygen molecules present in A during the given interval, dt, and M_{O_2} is the molecular weight of oxygen. Upon integrating this expression, it is found that

$$ln \frac{N}{N_O} = \frac{K}{\sqrt{M_{O_2}}} t,$$

where N_O is the number of oxygen molecules initially present. Since N and N_O are proportional to the final and initial partial pressures, respectively,

$$ln \frac{p_{O_2}}{p_{oO_2}} = -\frac{K}{\sqrt{M_{O_2}}} \cdot t.$$

Similarly, for hydrogen,

$$ln \frac{p_{H_2}}{p_{oH_2}} = \frac{K}{\sqrt{M_{H_2}}} \cdot t.$$

If t is the time necessary for the total pressure to fall to one half its initial value, t may be eliminated,

$$\frac{ln \frac{p_{O_2}}{p_{oO_2}}}{ln \frac{p_{H_2}}{p_{oH_2}}} = \frac{1}{4}.$$

Since

$$p_{oO_2} = p_{oH_2} = \tfrac{1}{2},$$

$$lnp_{O_2}^4 - lnp_{H_2} = ln\tfrac{1}{8},$$

$$\frac{p_{O_2}^4}{p_{H_2}} = \frac{1}{8},$$

---

[1] *Phil. Trans.*, **136**, 573 (1846).

and, since $p_{H_2} + p_{O_2} = \frac{1}{2}$,

$$p_{O_2}^4 + \frac{p_{O_2}}{8} = \frac{1}{16}.$$

Thermal Diffusion: The apparatus used by Reynolds[1] in his study of thermal diffusion is shown in Fig. 4. The two chambers, *A* and *B*, were connected by capillary tubes *E*, made of meerschaum, and also by a tube of comparatively large diameter, containing the tap *F*. *M* was a manometer. The chamber *B* was surrounded by ice and *A* by steam. A gas was introduced into the chambers, and, with the tap *F* open, equilibrium was obtained. When tap *F* was closed, the pressure in the hot chamber increased, as indicated by the manometer. The difference in pressure in the two vessels reached a definite amount, which was a maximum when the original pressure was of the order of one or two centimeters of mercury; at one atmosphere pressure, the difference was not perceptible. The lower the original pressure, the greater was the percentage difference in pressure, registered.

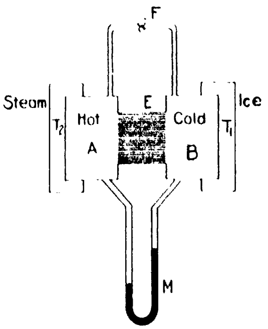

Fig. 4

If T_2 and T_1 were the temperatures of the hot and cold chambers respectively, then, when tap *F* was open and there was therefore no pressure difference, the number of molecules in *A* was inversely proportional to T_2, the number in *B* was inversely proportional to T_1. When tap *F* was closed, the number of molecules leaving *A* was proportional to the number present and also to their average velocity, i.e., proportional to $\frac{1}{T_2}$ and also to $\sqrt{T_2}$, or proportional to their product $\frac{1}{\sqrt{T_2}}$. Likewise, the number leaving *B* was proportional to $\frac{1}{\sqrt{T_1}}$. Since $\frac{1}{\sqrt{T_1}} > \frac{1}{\sqrt{T_2}}$, more left *B* than left *A*, and the pressure in *A* increased.

The problem of thermal diffusion has recently acquired considerable importance by reason of the possibility of its use in the separation of gaseous isotopes. It has been shown theoretically[2] and experimentally[3] that if a gaseous mixture is present in a container one portion of which is kept hot, and another cold, an equilibrium is attained in which there is an increased concentration of the larger or heavier molecules at the cold end and vice versa.

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[1] Reynolds, *Phil. Trans.* A 1879.

[2] Enskog, *Physik. Z.*, **12**, 538 (1911), *Ann. Physik*, **38**, 750 (1912). Chapman, *Phil. Trans.*, **217 A**, 115 (1916), *Phil. Mag.*, **34** 146 (1917).

[3] Chapman and Dootson *Phil. Mag.*, **33**, 248 (1917).

For a mixture of two isotopes, Chapman has deduced [1] a relation which has been given by Mulliken [2] in the form

$$\Delta_t x_2 = k_t ln \frac{T'}{T} = \frac{17}{3} \cdot \frac{M_2 - M_1}{M_2 + M_1} \cdot \frac{x_1 x_2}{9.15 - 8.25 x_1 x_2} ln \frac{T_1}{T}$$

for molecules which behave like elastic spheres. $\Delta_t x_2$ stands for the difference between the values of x_2 in the two temperature regions T' and T of molecules of mass M_1 and M_2 present in mol. fractions x_1 and x_2 originally. Actually in the case of a mixture of hydrogen and carbon dioxide, k_t is only about $\frac{1}{2}$ to $\frac{1}{3}$ as large as the above equation indicates since the molecules do not behave as elastic spheres. Actually thermal diffusion is a much weaker agent for isotope separation than ordinary diffusion. It has the advantage that it may be adapted to rapid continuous operation.

Maxwell's Law: The mean value of the molecular velocity which has been used in the derivation of the expression $p = \frac{1}{3}mnu^2$ is not the arithmetic mean of the velocities of all the molecules, but, as already defined, u is the velocity which, if possessed by all the molecules, would give rise to the same kinetic energy and the same pressure as that given by the gas with its random distribution of velocities. The problem of Maxwell's distribution law is to find out what fraction of all the molecules have any given velocity. That all of the molecules do not possess the same velocity requires no calculation, for, if, momentarily, they all did possess the same velocity, collisions would immediately disturb this uniform distribution. For the solution of this problem, recourse is had to the concept of probability. Since the number of molecules present in any measurable amount of a gas is so enormous, the results obtainable from probability considerations apply with great exactness. The expression for the distribution of velocities in a gas was first derived by Maxwell; later, by different procedures, by Boltzman, Jeans, and others. Many of the derivations have been criticized; one of the simpler ones is given here, the conclusions of which, at least, are beyond question.

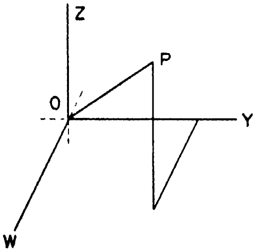

FIG. 5

The problem resolves itself into the following question. What fraction of the total number of molecules in a gas have velocities between x and $x + dx$. The velocities at any moment may be represented both in magnitude and direction by distances from the origin O (Fig. 5), the components of which are measured along the three axes W, Y, and Z, at right angles to each other. The length of OP for instance represents the velocity of a molecule which is moving in a direction parallel to OP; w, y, and z are the components of velocity along the chosen axes. The assumption is made that w, y, and z are independent of one another. The total number of molecules is denoted by n, and the number whose w-component of velocity lies between w and $w + dw$ is dn_1. This number is proportional to n, to dw, and also to some function of the component of the velocity w. Hence,

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[1] *Phil. Mag.*, **38**, 182 (1919).

[2] *J. Am. Chem. Soc.*, **44**, 1035 (1922).

$$dn_1 = nf(w)dw, \tag{14}$$

where f is some unknown function. If now dn_2 are the number of molecules having w-components of velocity lying between w and $w + dw$ and simultaneously having y-components lying between y and $y + dy$, then the same reasoning gives

$$dn_2 = dn_1 f(y)dy = nf(w)f(y)dwdy.^{1} \tag{15}$$

Similarly the number of molecules having simultaneously components of velocity lying between w and $w + dw$, y and $y + dy$, and z and $z + dz$ is given by

$$dn_3 = nf(w)f(y)f(z)dwdydz. \tag{16}$$

Each of this number of molecules will be represented by points similar to P (Fig. V), and, from the above reasoning, this number is proportional to the volume element ($dwdydz$), to n, and will depend also on some function of the distance, OP (that is on some function of x), but will be independent of the direction of OP. This last statement is based on the assumption that, at any moment, as many molecules of a gas are moving in one direction as in another. These facts are given by the expression

$$dn_3 = n\varphi(x)dwdydz = n\phi(x^2)dwdydz, \tag{17}$$

where φ and ϕ are functions of x such that $\varphi(x) = \phi(x^2)$.

$$f(w)f(y)f(z) = \phi(x^2) = \phi(w^2 + y^2 + z^2). \tag{18}$$

Differentiation with respect to w yields

$$f'(w)f(y)f(z)dw = \phi'(w^2 + y^2 + z^2)2wdw. \tag{19}$$

Division of equation (19) by (18) gives

$$\frac{f'(w)}{f(w)} = 2w\frac{\phi'(w^2 + y^2 + z^2)}{\phi(w^2 + y^2 + z^2)}.$$

Differentiation with respect to the other components and subsequent division gives the equations:

$$\frac{1}{2w}\frac{f'(w)}{f(w)} = \frac{1}{2y}\frac{f'(y)}{f(y)} = \frac{1}{2z}\frac{f'(z)}{f(z)} = \frac{\phi'(w^2 + y^2 + z^2)}{\phi(w^2 + y^2 + z^2)} = \text{const.} \tag{20}$$

---

[1] This step may need further amplification. The number of molecules having y-components between y and $y + dy$ is

$$dn = nf(y)dy$$

as before, but n molecules are no longer being considered, only those having w-components between w and $w + dw$, viz., dn_1.

The constancy of $\frac{\phi'(w^2 + y^2 + z^2)}{\phi(w^2 + y^2 + z^2)}$ is clear, for the first members of the series of equations (20) depend upon w, y, or z varying singly while $\frac{\phi'(w^2 + y^2 + z^2)}{\phi(w^2 + y^2 + z^2)}$ depends upon w, y, and z varying simultaneously. The function f must be such that it satisfies the above condition. By trial,

$$f(w) = ae^{-bw^2} \tag{21}$$

is found to do so, for

$$\frac{1}{2w}\,\frac{\frac{d(ae^{-bw^2})}{dw}}{ae^{-bw^2}} = \frac{-2abwe^{-bw^2}}{2wae^{-bw^2}} = -b, \tag{22}$$

in which expression a and b are constants. Then

$$f(w)f(y)f(z) = a^3e^{-b(w^2+y^2+z^2)} \tag{23}$$

or

$$\phi(x) = a^3e^{-bx^2}.$$

The constants, a and b, can be evaluated readily in terms of the average kinetic energy of the gas molecules. The number of molecules, dn, represented in Fig. 5 by points lying within a spherical shell of thickness dx and at a distance x from the origin is proportional to the volume of the shell $4\pi x^2dx$, to n, and to the function of x just evaluated. Hence,

$$dn = 4\pi a^3nx^2e^{-bx^2}dx, \tag{24}$$

$$\int_0^n dn = 4\pi a^3n\int_0^\infty x^2e^{-bx^2}dx,$$

$$n = 4\pi a^3n\frac{1}{4}\sqrt{\frac{\pi}{b^3}},$$

$$a = \sqrt{\frac{b}{\pi}}.$$

If the average kinetic energy of the molecule is given by $\frac{1}{2}mx_0^2$, then

$$\tfrac{1}{2}mnx_0^2 = \tfrac{1}{2}m\cdot 4\pi a^3n\int_0^\infty x^2x^2e^{-bx^2}dx,$$

$$x_0^2 = 4\pi a^3\frac{3}{8}\sqrt{\frac{\pi}{b^5}},$$

and, from the value of a found above,

$$b = \frac{3}{2x_0^2}.$$

Substitution of these values for a and b in equation (24) gives for the number of molecules, dn, having velocities between x and $x + dx$,

$$dn = 3\sqrt{\frac{6}{\pi}}\, n x_0^{-3} x^2 e^{-3x^2/2x_0^2} dx. \tag{25}$$

The average velocity of the molecule, x_1, is given by the expression

$$x_1 \int_0^n dn = 3\sqrt{\frac{6}{\pi}}\, n x_0^{-3} \int_0^\infty x \cdot x^2 e^{-3x^2/2x_0^2} dx,$$

$$x_1 = 3\sqrt{\frac{6}{\pi}}\, x_0^{-3} \frac{2x_0^4}{9},$$

$$x_1 = \sqrt{\frac{8}{3\pi}} \cdot x_0 = 0.92 x_0.$$

If equation (25) is used to plot numbers of molecules against their velocities, a curve of the form shown in Fig 6 is obtained. The total number of molecules is given by the area included between the curve and the axis of x. The total number of molecules is given by the integral

$$\int_0^\infty \alpha x^2 e^{-\beta x^2} dx, \tag{26}$$

where α and β are constants at a given temperature. The form of equation (26) shows that there are few molecules having velocities that are very large or very small. A calculation shows that over ninety per cent of them have velocities lying between $\frac{1}{4}x_1$ and $\frac{7}{4}x_1$, corresponding to the area $ABCDE$ in Fig. 6

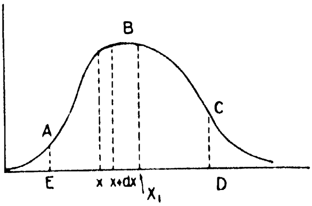

Fig. 6

It is now necessary to consider what effect the idea of the variation of molecular velocities has on the derivation of the ideal gas law and the deductions made so far. The pressure exerted by one molecule moving with velocity x_1 in unit volume was shown to be $\frac{1}{3}mx_1^2$. Suppose a second molecule is present with velocity x_2, then the total pressure will be

$$\tfrac{1}{3}mx_1^2 + \tfrac{1}{3}mx_2^2.$$

Hence if there are n molecules present,

$$p = \tfrac{1}{3}m \sum_{a=1}^{n} x_a^2 = \tfrac{1}{3}mnx_0^2,$$

where

$$x_0 = \frac{x_1^2 + x_2^2 + \cdots}{n}.$$

Hence, the equation $pv = \frac{2}{3}E$ is not affected. The velocity of gas molecules calculated from the expression $pv = \frac{1}{3}mnx_0^2$ does not give the average velocity. From the deductions made by Maxwell it is seen, however, that the average velocity x_1 is given by

$$x_1 = \sqrt{\frac{8}{3\pi}}\,x_0 = \sqrt{\frac{8}{3\pi}}\sqrt{\frac{3pv}{M}} = \sqrt{\frac{8}{\pi}\frac{pv}{M}}, \qquad (27)$$

and the important point to note is that the average velocity differs from the velocity thus far considered by a constant which is independent of the nature of the gas. Hence, the conclusions as to the relative rates of diffusion of gases through capillary tubes are not affected by the variation of molecular velocities.

When a gas expands into an evacuated space (case II, Fig. 1), it is probable that the faster moving molecules will enter this in greater numbers than the slower moving ones and thus the temperature in the newly filled space will be higher for a brief time before equilibrium is established; when this is attained no temperature change will be found to have occurred.

Effect of Gravity on Gas Law: The probability of uniform distribution of the molecules of a gas *in an isolated space* is inherent in the molecular theory, on the supposition that the number of molecules per cubic centimeter is exceedingly great. This is not the case and not to be expected in a gravitational field. Consider a molecule oscillating through a distance dS between the top and bottom of a flat box. Let its velocity, when it passes through the center of the distance dS, be X. The time taken for the molecule to reach the top or bottom from this point is $\frac{dS}{2X}\cdot$ Due to the effect of gravity its velocity at the bottom will be $X + g\frac{dS}{2X}$ and at the top it will be $X - g\frac{dS}{2X}\cdot$ Since the pressure is given by the change of momentum times the number of impacts, the pressures at the bottom and the top will be given respectively by

$$2m\left(X + g\frac{dS}{2X}\right)\cdot\frac{X}{2dS} \qquad \text{and} \qquad 2m\left(X - g\frac{dS}{2X}\right)\frac{X}{2dS}\cdot$$

Hence, the difference in pressure between the top and bottom is mg, the weight of the gas molecule.

Therefore, in a gas, the pressure must gradually decrease from layer to layer with increasing distance from the earth's surface. The pressure at any point is greater than the pressure at a point higher up by an amount equivalent to the weight of the gas between. The variation in pressure with distance is, therefore, readily calculated.

The density ρ of a gas is defined as the weight of one cubic centimeter. This quantity varies therefore with the temperature and pressure, the connection between the three being given in a convenient form by substituting the specifications of the definition in the gas law $pv = \frac{m}{M}RT$, where $R = 0.082$ when

p is measured in atmospheres and v in liters. That is,

$$p(0.001) = \frac{\rho}{M} RT$$

or

$$\rho = \frac{pM}{1000RT}. \tag{28}$$

Now, let p_0 be the pressure at the earth's surface and p be the pressure at height h. At a distance $h + dh$, let the pressure be $p - dp$. It follows from the preceding that, if p is expressed in grams per sq. cm.,

$$-dp = \rho dh,$$

or, if p is expressed in atmospheres, and ρ in grams per cc.,

$$-1033dp = \rho dh, \tag{29}$$

where ρ is the density at height h and dh is small. Substituting in this equation the value for ρ given in (28), there results the expression

$$-1033dp = \frac{pM}{1000RT}dh.$$

This equation has been found to hold over a range where the force of gravity can be taken as constant. On integration, it follows that

$$ln\frac{1}{p} = \frac{M}{1{,}033{,}000RT}h + I. \tag{30}$$

The integration constant I may be evaluated by setting $p = p_0$ when $h = 0$, whence

$$ln\frac{1}{p_0} = I$$

and

$$ln\frac{p_0}{p} = \frac{M}{1{,}033{,}000RT}h.$$

Specific Heats of Gases: The energy of a gas at temperature T is given by the equation of the kinetic theory

$$E = \tfrac{3}{2}pv = \tfrac{3}{2}RT.$$

By definition, the specific heat of one gram mol. of a gas at constant volume is

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = \tfrac{3}{2}R = 2.97 \text{ calories.} \tag{31}$$

Upon this basis, the molecular heat of a gas should be independent both of the temperature and the nature of the gas. This has been confirmed for all monatomic gases so far examined within a wide temperature range, the gases including helium, argon, krypton and mercury vapor.[1] The use of the "explosion method" of Berthelot[2] by Nernst[3] and coworkers (see Chapter VI) has permitted such measurements to be carried beyond 2000° C. With monatomic gases the above conclusion is verified even at these extreme temperatures. Low temperature measurements by Eucken[4] on helium have shown that the same holds true with this gas at the temperature of liquid hydrogen.

For all gases other than monatomic gases, the heat capacity at constant volume is generally greater than $\frac{3}{2}R$ and it varies with temperature. The simple kinetic theory is inadequate to the explanation of this, and, as a consequence, additions to the theory become imperative. The additions take the form of assumptions with regard to the nature and structure of the molecules. The interpretation of specific heat measurements is impossible so long as the molecule is regarded as a mathematical point.

The principle underlying the discussion of the specific heat of gases from the standpoint of molecular kinetics is known as the principle of equipartition of energy deduced by Maxwell and Boltzmann making use of statistical mechanics. The principle asserts that in a system such as a gas composed of innumerable moving parts, energy will be distributed equally along every degree of freedom. Degree of freedom is the name given to each possible mode or possible direction of motion of a molecule. According to Maxwell, the motion of a monatomic gas molecule which is moving freely in space can be fully described by three momentary components of its velocity along three axes of a coordinate system in space, each axis at right angles to the other. In such circumstances the molecule possesses, according to Maxwell, a threefold freedom of translatory motion or, alternatively, has three degrees of freedom. The energy of a molecule resolved into these three components w, y and z is

$$\tfrac{1}{2}mw^2 + \tfrac{1}{2}my^2 + \tfrac{1}{2}mz^2.$$

For all the molecules present in a given space it follows from the discussion in preceding sections that

$$\tfrac{1}{2}mw^2 = \tfrac{1}{2}my^2 = \tfrac{1}{2}mz^2 = \tfrac{1}{2}pv = \tfrac{1}{2}RT. \qquad (32)$$

A quantity of energy equal to $\frac{1}{2}RT$ is therefore assigned to each of the three degrees of freedom of translatory motion of the monatomic gas, corresponding, therefore, as already set forth, to a heat capacity of $\frac{3}{2}R$ calories. Any gas molecule whether monatomic, diatomic or polyatomic may possess translatory motion with three degrees of freedom, may have, therefore, energy in virtue of translatory motion equal to $\frac{3}{2}RT$ or heat capacity in virtue of translatory energy equal to $\frac{3}{2}R$ calories.

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[1] For the technique of such specific heat measurements, see Chapter VI, where several methods are given as well as some of the experimental results.

[2] *Compt. rend.*, **95**, 1280 (1882), *Ann. Chim. Phys.*, (6) **4**, **17** (1885).

[3] Pier, *Z. Elektrochem.*, **15**, 536 (1909).

[4] *Ber. d. physik. Ges.*, **18**, 4 (1916).

With other than monatomic gases, at least two other types of motion must be considered. The two atoms in a diatomic molecule may possess an intramolecular motion of the two atoms with respect to one another, a type of motion giving rise to what may be termed vibrational energy. Such energy will be both kinetic and potential. The motion will be unidirectional or linear, along the axis of the diatomic molecule. On the Maxwell concept, therefore, one degree of freedom would be assigned to such motion. With a triatomic molecule it is evident that there would be three directions along which such linear vibrations could occur, and, hence, three degrees of freedom might therefore be expected.

In addition to translatory and vibratory motion there is also the possibility that a gas molecule possesses energy of rotation. Even monatomic molecules, since they have volume, may possess rotatory motion in addition to translatory motion. There may be a spin of the molecule as a whole about its center of gravity. That any energy accruing to a monatomic molecule from such motion is small is obvious from the fact already stated that, over a wide temperature range, the heat capacity of a monatomic gas is $\frac{3}{2}R$ calories corresponding to the three degrees of freedom of translatory motion. The reason for the absence of rotational motion in a monatomic gas is not yet clear, though the application of quantum theory may serve to elucidate this point in the future (see Chapter XVI). A diatomic molecule should possess rotatory motion brought about by collision with other molecules. The two atoms of the molecule would describe, as a result of collision, circular orbits around the center of gravity of the molecule. The motion would be two-directional, resolvable along two axes at right angles to one another. Two degrees of freedom might therefore be assigned to such motion. For a triatomic gas, in which all the atoms were situated along a given axis, two degrees of freedom of rotational motion would be possible. In three-dimensional arrangements of the atoms with respect to one another three degrees of freedom of rotational motion might be anticipated.

Experimental measurement shows that diatomic gases have varying values for the molecular heat at ordinary temperatures and show an increase with increasing temperature; this is evident from the following data for typical diatomic gases.

The explanation of these results is by no means established. It is generally agreed that diatomic molecules possess three degrees of freedom in virtue of translation. Two degrees of freedom may be assigned to the molecule in virtue of rotational motion. Kruger[1] would deny the possibility of rotation but would substitute a motion which may be termed "precessional vibration," the molecule possessing gyroscopic properties brought about by reason of molecular collisions. It is customary also to ascribe to a diatomic molecule a degree of freedom in virtue of linear vibration of one atom with respect to the other. Vibratory motion involves both kinetic and potential energy to each of which an energy quantity equal to $\frac{1}{2}RT$ might be assigned. From translation and vibration an energy quantity $\frac{5}{2}RT$ would result, corresponding to a heat capacity of $\frac{5}{2}R = 5$ cals. per mol. per degree. From translatory and rotational energy alone a heat capacity of 5 cal: per mol. per degree would also result. If rotational and vibrational energy were both included, the quantities would be raised to $\frac{7}{2}RT$ for the energy and $\frac{7}{2}R = 7.0$ cals. per mol. per degree for the heat capacity.

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[1] *Gött. Nachr.*, 1908. *Ann Physik*, (4) **50**, 346 (1916), **51**, 450 (1916).

TABLE I

Molecular Heats at Constant Volume between t_1° and t_2° C.

Hydrogen:	C_v (18° C.);	4.87 [1]
	C_m (0–2200° C.);	$4.76 + 0.000038t$ [2]
	C_m (0–2500° C.);	$4.700 + 0.000045t$ [3]
Nitrogen:	C_m (0–2500° C.);	$4.900 + 0.00015t$ [3]
Oxygen:	C_m (0–2500° C.);	$4.900 + 0.00015t$ [3]
Hydrogen Chloride:	C_m (0–2200° C.);	$4.98 + 0.000018t$ [2]
Chlorine:	C_v (18° C.);	6.00 [2]
	C_m (18–627° C.);	6.689 [2]
	C_m (18–1027° C.);	6.820 [2]
	C_m (18–1427° C.);	6.895 [2]
	C_m (18–2327° C.);	6.981 [2]

[1] Landolt-Bornstein Tabellen, 1923.

[2] Wohl, *Z. Elektrochem.*, **30**, 36, 49 (1924) This paper gives a full treatment of the mean molecular heats of hydrogen, chlorine and hydrogen chloride from the standpoint of experiment and quantum theory of gases.

[3] Pier, *Z. Elektrochem.*, **16**, 898 (1910).

For triatomic gases, in a similar manner, one might expect three degrees of freedom in virtue of translation, three in virtue of rotation, three in virtue of vibration, from three pairs of vibrating atoms, this latter motion involving both kinetic and potential energy. Translation and vibration should give a heat capacity of 9 cals. per mol. per degree; translation, vibration and rotation should give a value of 12 cals. per mol. per degree. Typical triatomic gases vary widely from this prediction. Water vapor at 50° C. has a molecular heat of about 6 cals. and at 2000° C. about 10 cals. Carbon dioxide has a heat capacity of 7 cals. at room temperature and 10.5 cals. at 2000° C.

The continuous variation of heat capacity with temperature is not explicable on the basis of the principle of equipartition of energy. Equipartition would involve a constant molecular heat or at least a step-wise change in molecular heat by $R/2$ cals. as a new degree of freedom involving a new type of energy became established. The quantum theory has been invoked, therefore, to account for the continuous nature of the increase in heat capacity with temperature. It has been assumed that the rotational and the vibrational energy are acquired by quanta.[4] Eucken's determinations of the molecular heat of hydrogen at low temperatures[5] show that at 35° K. the molecular heat has fallen to 3 calories, that of a monatomic gas. Hydrogen in this state is evidently devoid of both vibrational or rotational energy. The molecular heat at 473° K. is 4.96 which would correspond to three degrees of translatory motion and two of rotational energy. In the interval between 35° K. and 473° K. it is assumed that the rotational energy is acquired in quantum steps.

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[4] See Chapter XVI. Also, Bjerrum, *Z. Elektrochem.*, **17**, 731 (1911); **18**, 101 (1912). Wohl, *Z. Elektrochem.*, **30**, 36, 49 (1924).

[5] *Ber. d. physik. Ges.*, **18**, 4 (1916).

Mean Free Path: That a gas molecule has a definite volume is borne out by experimental evidence other than that dealing with specific heat measurements. When two gases are brought in contact with one another, uniform mixing by diffusion of the gas molecules requires a length of time quite out of proportion to that which one would expect from a calculation of molecular velocities. This is due to the frequency with which collisions occur. If X_0 is the average velocity of a gas molecule, then a brief consideration will show that there will be many encounters with other molecules while the molecule travels through this distance X_0. Consequently, its path is in the form of a zig-zag by reason of which a molecule may at the end of a second be close to the point from which it started. The average distance a molecule travels between two collisions is called the mean free path. If r is the radius of a sphere which gives the average effective form of a molecule, then a collision occurs with another molecule when the center of one reaches the surface of a sphere of radius $2r$ surrounding the first. The chance of one molecule hitting another is therefore proportional to the projected area of the others, namely, $4\pi n r^2$, where n represents the number of molecules per cubic centimeter. The greater the chance for a collision the smaller will be the free path and hence the free path l is inversely proportional to the chance of a collision occurring

$$l = \frac{k}{4\pi n r^2} = \frac{1}{\sqrt{2}\,4\pi n r^2}\,. \qquad (33)$$

The proportionality constant k has been estimated to be $\frac{1}{\sqrt{2}}$ by Maxwell.[1] Tait[2] obtained a different value for this constant. This factor has to be corrected still further for the tendency of the direction in which a molecule moves to persist after collision has taken place. These calculations are beyond the scope of this chapter.

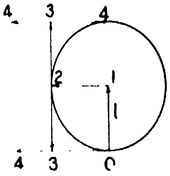

Fig. 7

It is possible to get an estimate of the average distance a molecule will move in a second from its starting point. Suppose a molecule starts from a point O, Fig. 7, and at the end of the free path a collision occurs, then the direction after the collision may be any one so that the molecule at the end of its second free path will be at any point on the circle, radius l. For instance, if the molecule just touches the one it collides with, then its distance from O will be $2l$, if it collides head on it will return to O and its total displacement at the time of the second collision will be zero. The average square displacement S^2 from O will be $2l^2$. Working on the plan of these averages, the third collision will give as the average square displacement

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[1] Jean's Dynamical Theory of Gases, pp. 35, 250. Cambridge U. Press.

[2] Tait, *Roy. Soc. Edin. Trans.*, **33**, 74 (1886).

$$S_3^2 = \frac{\{(2l)^2 + l^2\} + l^2}{2} = 3l^2.$$

The probability of this is made manifest by the diagram, Fig. 7, since it is equally probable that the molecule will occupy either of the two positions 3 at the moment of the third collision. Similarly the chances are equal that it will occupy any one of the positions 4 at the time of the fourth collision, so that

$$S_4^2 = \frac{\{(2l)^2 + (2l)^2\} + (2l)^2 + (2l)^2 + 0}{4} = 4l^2.$$

Generally at the nth collision $S^2 = nl^2$.

In one second, the number of collisions are equal to $\frac{x_1}{l}$, where x_1 is the average velocity of the molecules. Hence, at the end of one second,

$$S^2 = \frac{x_1 l^2}{l} = x_1 l, \qquad (31)$$

or the product of the average velocity and the mean free path. The average displacement is less than the average square displacement. Hence, although a hydrogen molecule travels with the velocity of 1.6×10^5 cms. per sec., since l is of the order 10^{-5} cm. the average displacement of the hydrogen molecule is less than one centimeter per second. The average displacement is of course greatly exceeded by a small number of molecules, for both the free path and molecular velocity vary enormously. That the average rate of diffusion of gases is small is, however, not surprising.

Assuming that n is known from electrolysis and from the value of the unit of electricity (see Chapter I, p. 20), there are two unknowns in the equation $l = \frac{1}{\sqrt{2}\, 4\pi n r^2}$, so that r must be determined before l can be estimated. It may be pointed out that l is independent of the temperature according to this relationship. Experimental examination has shown that this is not the case but this disagreement is in accord with another important property inherent in the molecules. Before considering this, the next section will show how the mean free path may be measured.

Viscosity: Viscosity of a fluid is a term applied to the inner friction which tends to bring to rest portions of the fluid which are moving relative to one another. The coefficient of viscosity is defined as the force which, when applied tangentially to each square centimeter of a plane of a fluid at a distance of one centimeter from a parallel plane of the fluid, will give a uniform velocity of one centimeter per second to the first plane relative to the second. If η is the coefficient of viscosity, it follows that

$$F = \eta \frac{dx}{ds}, \tag{35}$$

where F is the force applied per unit area of a plane whose velocity x varies with respect to a neighboring plane ds units distant.

The definition of the coefficient of viscosity is cumbersome. Its meaning may be perhaps elucidated by an application to a problem dealing with the experimental method[1] of measuring the viscosity of a fluid by its rate of flow through a narrow tube. It is assumed that the fluid flows in stream lines, without turbulent motion, along the tube, a condition which is in agreement with experimental evidence providing the diameter of the tube is limited to a certain range depending on the viscosity of the fluid. Let P be the difference in pressure per square centimeter between two ends of a tube of radius R and length L. Due to viscosity, the cylindrical shell of fluid quite close to the walls of the tube will be at rest, the rate of flow of cylindrical shells increasing the nearer to the center. Consider a cylindrical shell, radius r, moving with a velocity x. The area of the cylindrical shell is $2\pi rL$, and, hence, the tangential force acting on the cylinder opposite to the direction of flow is $-2\pi rL\frac{dx}{dr}\cdot\eta$. The minus sign signifies that as r (which is measured from the center) increases, x diminishes. The force acting on the end of the cylinder is $P\pi r^2$. When equilibrium has been established, the flow of liquid through the tube is uniform and these two forces must balance, so that

$$P\pi r^2 = -2\pi rL\frac{dx}{dr}\eta,$$

$$x = \frac{-P}{2L\eta}\,\frac{r^2}{2} + I.$$

When $r = R$, $x = 0$. Hence,

$$x = \frac{P}{4L\eta}(R^2 - r^2).$$

This expression gives the velocity, at steady flow, of the cylindrical shell of radius r.

It is difficult to measure the velocity of flow at any particular point, but the total volume W flowing through the tube per second can be readily determined. This is given by

$$W = \int_0^R 2\pi rx\,dr = \frac{\pi P}{2L\eta}\int_0^R r(R^2 - r^2)dr$$

$$= \frac{\pi P r^4}{8L\eta}. \tag{36}$$

η can therefore be determined by measuring P, W, r, and L.

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[1] Poiseuille, *Compt. rend.*, 15, 1167 (1842).

In the case of a gas the determination of the viscosity is attended by many difficulties. Poiseuille's equation is the basis of the experimental method. The diameter of the tube through which the gas is forced must have a certain limiting value to prevent turbulence, and certain corrections have to be applied for the expansion of the gas.[1]

The viscosity of a gas gives a measure of the mean free path of its molecules. That this is true can be demonstrated by the following argument. Two parallel planes, A and B, in a gas are at a distance l apart, where l is the mean free path. If the matter in plane A has a velocity dy relative to the matter in plane B, then the tangential force per square centimeter on A with reference to B is $\eta \frac{dy}{l}$. The number of molecules contained in a section of one square centimeter and bounded by the two planes is ln, where n is the number per cubic centimeter, and $\frac{1}{3}ln$ molecules may be considered as oscillating between the two planes. When a molecule leaves plane A, its velocity component in a direction of mass flow of the gas is greater by dy than that of the molecules in plane B, so that when it reaches plane B its momentum is decreased by $m \cdot dy$ and the momentum of plane B is increased by that amount. On its return to plane A, $m \cdot dy$ is the momentum given up in the tangential direction; hence, the change of momentum in a tangential direction is $m \cdot dy$ multiplied by the number of impacts, $\frac{X_1}{l}$, where X_1 is the average velocity of the molecules. Hence, the total change in momentum in a tangential direction is a measure of the tangential force between the planes A and B, and is given by

$$\frac{n}{3} l \frac{X_1}{l} m dy = \tfrac{1}{3} nmX_1 \frac{dy}{l} \cdot l = \eta \frac{dy}{l},$$

so that

$$\eta = \tfrac{1}{3} nX_1 lm = \tfrac{1}{3} \rho X_1 l, \tag{37}$$

where ρ is the density of the gas. Since X_1 can be calculated from the temperature, it follows that a measurement of the viscosity enables one to calculate the mean free path.

Maxwell[2] was the first to point out that, in agreement with the preceding equation, the viscosity of a gas is independent of the pressure. Thus, doubling the pressure will double the density. On the other hand, the mean free path will be halved. This has been verified within the obvious limits given by the dimensions of the apparatus which must be considerably greater than the mean free path itself.[3] Since the velocity of a gas molecule is proportional to the square root of the temperature, it follows from the above relationship that the viscosity is proportional to the square root of the absolute temperature. This has not been found to be the case; the viscosity increases with the temperature in marked contrast to liquids whose viscosities decrease with increase of temperature. The increase of gaseous viscosity is more rapid than the one half power of the temperature, which means that the mean free path must increase with rise in temperature. This is, as will be seen shortly, of the greatest importance in connection with the molecular theory of gases.

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[1] Schultze, *Ann. Physik*, **5**, 140 (1901).

[2] Maxwell, *Phil. Trans.*, **156**, 249 (1886).

[3] Millikan, *Phys. Rev.*, **21**, 217 (1923).

In the following table the viscosities for a number of gases at 0° C. are given, together with the mean free path calculated by the above relationship. More exact results are obtained by taking into account the persistence of direction of movement and other corrections of a rather complicated nature. The values thus obtained are 33 per cent smaller than those given here.

TABLE II

VISCOSITIES AND MEAN FREE PATHS AT 0° C.[1]

	$\eta \times 10^6$	X_1	$p \times 10^6$	$l \times 10^6$
He	189	121 000	179	26 1
H_2	85	170,000	89	16 7
CO	163	15,400	1260	8.5
N_2	167	15,400	1260	8 7
O_2	192	12 500	1130	9 5
Ar	211	38,000	1790	9 3
CO_2	139	36,200	1970	5.8

[1] Values for viscosities determined by Kia-Lok Yen *Phil Mag* **38**, 582 (1919), Breitenbach, *Ann Physik*, **5**, 166 (1901), K Schmitt, *Ann Physik* **30**, 310 (1909), Graham, *Phil. Trans.*, 8 (1846), Schultze, *Ann Physik*, **5**, 140 (1901), *Cf.* Jeans, Dynamical Theory of Gases, p 288

Conduction of Heat: The mechanism of the conduction of heat through a gas is intimately connected with the phenomenon of the mean free path. In a gas, the space between a hypothetical plane A, maintained at a temperature $T + 1°$, and B, maintained at a temperature $T°$, may be imagined as being divided up into sections 1, 2, 3, ···, etc., by parallel planes distant l from one another, where l is the mean free path. Before equilibrium has been established the molecules in section 1 next to plane A have a velocity greater than that of the molecules in the other sections. A molecule starting from plane A and meeting a molecule from section 2 will share its velocity with the latter upon colliding, so that this molecule will now have a velocity corresponding to $T + \frac{1}{2}°$. At the end of its path this velocity will be given to a molecule in section 3, and so on, with the result that, if the molecules of a gas were only moving in a direction perpendicular to the planes, the rate at which the increased energy of the molecules in section 1 would travel would be proportional to x_1, the average velocity corresponding to a temperature $T + \frac{1}{2}°$. But, since only one third of the molecules in each section may be looked upon as transferring energy in this direction, and since they must come into temperature equilibrium with all the molecules in their section, the increased energy has to travel at right angles in each section and is thus diffused. The greater the number of sections the lower will therefore be the rate at which the increased energy will travel in the direction perpendicular to the planes and this rate is therefore proportional to x_1l. But, it is not solely the energy due to increased velocity which travels in the direction from A to B in the case of molecules composed of two or more atoms. The rotational energy is in equilibrium with the translatory energy and, providing this equilibrium is established rapidly, the amount of energy which finds its way from A to B per second will be proportional to the rate x_1l and to Nn, where n is the number of molecules per cubic centimeter and N the degrees of freedom of one molecule.

Specific thermal conductivity, K, is defined as the number of calories required to enter unit area of plane A in order that the temperature of planes A and B may remain constant, at $T + 1°$ and T respectively, when the planes are unit distance apart. Hence,

$$K = klx_1Nn.$$

Since the velocities of the molecules of various gases at the same temperature are inversely proportional to the square root of their molecular weight M, a comparison of the thermal conductivities should be given by

$$K = k'\frac{lN}{\sqrt{M}}. \tag{38}$$

TABLE III[1]

COMPARISON OF THERMAL CONDUCTIVITIES

	$K \times 10^6$	N	M	k'
He . .	336.0	3	2.00	8.6
H_2 .	397.0	5	1.41	6.8
CO .	51.2	5	5.29	6.7
N_2 . .	56.6	5	5.29	6.8
O_2 . . .	57.0	5	5.66	6.8
Ar . . .	39.0	3	6.32	8.8
CO_2 .	33.7	6	6.63	6.5

[1] Values for *l* taken from Table II, heat conductivities, Eucken, *Physik. Z.*, **14**, 324 (1913); Schwarze, *Ann. Physik*, **11**, 303 (1903).

The constant k' is seen to be the same for diatomic gases but has a larger value for monatomic gases. The explanation for this is perhaps to be found in the fallacy of assuming that equilibrium is instantaneous. Thus, if 8.7, the constant for a monatomic gas, is correct, N for a diatomic gas would be $3 + 2\epsilon$, where ϵ is a fraction indicating that the increase in rotational energy corresponding to the increase in translatory energy has lagged behind. The possibility of this has already been touched on in the discussion of the specific heats of gases. There too it was indicated that, at very low temperatures, a diatomic molecule behaves as a monatomic molecule from the point of view of energy content. The thermal conductivity of hydrogen has been examined[1] at very low temperatures and there the value $N = 3$ is required to give a value 8.7 to k'. This, then, is in good agreement with the specific heat measurements.

Attractive Forces between the Molecules: The subject matter of this section may be conveniently introduced by considering the variation of viscosity of a gas with the temperature. As has been mentioned before, the viscosity formula presents certain discrepancies inasmuch as experimental results are not in agreement with the theoretical relationship that

$$\eta = \tfrac{1}{3}\rho c_1 = k\rho l\sqrt{T}.$$

Sutherland[2] found that the relationship

$$\eta = \frac{k\rho l\sqrt{T}}{1 + \frac{C}{T}}, \tag{39}$$

more truly represents the experimental facts. Thus, l is proportional to $\left(1 + \frac{C}{T}\right)$, or, in other words, the free path, l, increases with lowering of the temperature. Furthermore, the value of C is not a universal constant but varies markedly from gas to gas, having the smallest value for helium and increasing markedly in the order, hydrogen, nitrogen, oxygen, carbon dioxide. The question as to what is the cause of the increase in the mean free path with rise in molecular velocity can be answered by assuming that attractive forces exist between the molecules. It is obvious that the number of collisions between the gas molecules will be increased and therefore the mean free path decreased by such forces. It is also obvious that the greater the velocity of the molecule, the smaller will be the effect of such a force in tending to deflect the molecule from its path so as to cause a collision with another. Thus, the existence of forces of mutual attraction will explain the variation of the mean free path with the temperature.

It must be pointed out that the explanation given above is not the only possible one. The mean free path is inversely proportional to the square of the diameter of the molecules. If the molecules are compressible, their average diameter will be decreased with rise in temperature due to the greater impact on collision, with the result that the mean free path will be increased. As will be seen later, the compressibility of the molecules may play a part in the variation of the mean free path, but what is known of the compressibility of the molecules makes it impossible to account for the value of C in Sutherland's equation. The experimental values of C are far too large to be accounted for by the compressibility of the molecule, and the values of C for various gases are by no means in the same order as the compressibilities. Hence, the first explanation is probably the correct one.

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[1] Eucken, *Sitz. preuss. Akad. Wiss.*, 141 (1912).

[2] Sutherland, *Phil. Mag.*, (5) **35**, 507 (1893).

The relative values of C for various gases show that the forces are by no means in the nature of gravitational forces, that is, they are not dependent on the relative masses of the molecules. The forces are specific, and depend, from the point of view of the modern theory of the structure of the atom, on the relative distributions of the electrons and the positive nuclei in the molecule; that is to say, these forces of attraction are chemical forces.

The variation of the mean free path with the temperature is of course by no means the only evidence of the existence of molecular forces. Deviations from the ideal gas law, changes in temperature upon the expansion of gases when no external work is performed, liquefaction of gases, all are evidence of the existence of attractive forces between molecules. Actually, it will be seen that the essential difference between a liquid and a gas is due to the fact that a liquid is matter existing under conditions such that the attractive forces predominate in determining the properties of matter in this state.

Viscosity and Molecular Diameter: Rankine has employed his experimental determinations of gaseous viscosities in the calculation of the radius of a variety of gas molecules.[1] Maxwell's equation connecting viscosity and mean free path is

$$\eta = \tfrac{1}{3}\rho l x_1,$$

where x_1 is the average velocity of the molecules. More correctly, the equation may be written

$$\eta = 0.307\rho l\sqrt{\frac{3p}{\rho}},$$

where $\sqrt{\frac{3p}{\rho}}$ is equal to the root mean molecular velocity. Similarly the Maxwellian equation connecting the mean free path l and the radius is (*cf.* equation 33)

$$l = \frac{1}{4\sqrt{2}\, n\pi r^2},$$

n being the number of molecules per cubic centimeter of gas. If, now, one substitutes in this equation the Sutherland expression for the true radius r_0 by means of the equation

$$\frac{r_0^2}{r^2} = 1 + \frac{C}{T},$$

it is possible to derive the value of r_0 from measurements of gaseous viscosity with the aid of the three equations given. Rankine utilized this method in his earlier work and obtained values for the inert gases varying from helium $= 0.84 \times 10^{-8}$ cm. to xenon $= 1.53 \times 10^{-8}$ cm.

Considerable interest now attaches to such measurements, since, by use of X-ray analyses of crystals, data on molecular distances and radii are being directly obtained. (See Chapter V.) Rankine has therefore extended his measurements recently making use of a somewhat more complex formula, developed by Chapman,[1] of the form

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[1] *Proc. Roy. Soc.*, **83**, 516 (1910); **84**, 181 (1910); **86**, 162 (1912); **91**, 201 (1915); *Phil. Mag.*, **29**, 552 (1915); **40**, 516 (1920); **42**, 601, 616 (1921); **44**, 292 (1922).

$$4\pi r_0^2 = \frac{0.491(1+\epsilon_a)\rho\overline{V}}{\sqrt{2}\,n\eta\left(1+\frac{C}{T}\right)}, \tag{40}$$

where the symbols have the same significance as above, $\overline{V}$, however, being the mean molecular velocity, $(1+\epsilon_a)$ a constant which in all cases investigated does not differ by one per cent from unity. Rankine has shown that his measurements of molecular diameters so calculated from experimental determinations of viscosity are, in the main, in agreement with the modern concepts of molecular make-up as suggested by the Lewis-Kossel-Langmuir theory of the atom. They serve also as confirmatory evidence for molecular magnitudes deduced from crystallographic analysis by the X-ray method. The following table gives some comparative data

TABLE IV

MOLECULAR RADII FROM CRYSTAL MEASUREMENTS AND GASEOUS VISCOSITIES

Gas	Radius (Bragg)	Radius (Rankine)	Gas	Radius (Bragg)	Radius (Rankine)
Helium		0.94×10^{-8} cm	Hydrogen Fluoride	0.65	1.17
Neon	0.65×10^{-8} cm	1.17	Hydrogen Chloride	1.02	1.43
Argon	1.02	1.43	Hydrogen Bromide	1.17	1.58
Krypton	1.17	1.59	Hydrogen Iodide	1.35	1.75
Xenon	1.35	1.75			

Apparent Deviations from the Ideal Gas Law: The variation of the density of a gas with distance from the earth's surface has already been accounted for by the effect of gravity. The other apparent discrepancies in the gas law were of a more serious nature at a time when the fundamental truth of Avogadro's hypothesis was not realized. Thus, the measurements of Dumas[2] seemed to show that sulphur vapor, iodine vapor, ammonium chloride, and a number of other vapors did not conform with the equation

$$pv = NRT.$$

Thus, ammonium chloride, in the vapor state, gave pressures greatly exceeding those calculated from the above equation.

In the case of ammonium chloride the abnormally high pressure can be accounted for by the dissociation of the molecules in the vapor state into ammonia and hydrogen chloride according to the equilibrium

$$NH_4Cl \rightleftarrows NH_3 + HCl.$$

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[1] *Phil. Trans.*, **216**, 347 (1916).

[2] *Ann. Chim. Phys.*, (2) **33**, 337 (1826).

If this chemical equilibrium exists and α is the fraction of ammonium chloride dissociated, the total number of gram molecules present will be $n(1 + \alpha)$, so that

$$pv = n(1 + \alpha)RT$$

and the gas law is found to hold when the chemical dissociation α is taken into account.[1] That this chemical dissociation actually occurs is proven by diffusion experiments carried out with the apparatus represented in Fig. 3. It was found that the gas which diffused through the capillary tube contained an excess of ammonia. This can only be the case if the ammonium chloride is split up into hydrogen chloride and ammonia molecules, in which case the lighter ammonia molecules would diffuse more rapidly. Similar phenomena of chemical association and dissociation were found to occur in the gases investigated by Dumas.

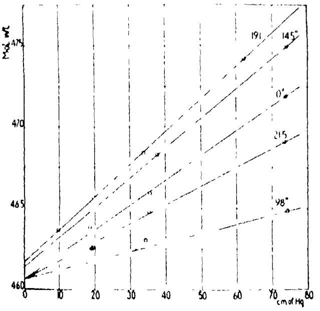

Fig. 8. Isothermal Molecular Weight Curves for Methyl Ether

Real Deviations from the Ideal Gas Law: With increased refinement in experimental technique it was found that the gas laws of Boyle and Gay Lussac did not hold exactly. For any given gas, the magnitude of the discrepancy increased with increase in pressure and lowering of temperature, with every indication that the gas law would hold exactly only at infinite dilution of the gas. As an example of the magnitude of the variation, a number of values for M for methyl ether, determined at various temperatures and pressures, and calculated on the basis of the ideal gas law $pv = \frac{m}{M} RT$, are given in Table V, and represented in the accompanying diagram, Fig. 8.

TABLE V

Temp.	Pres.	M	Temp.	Pres.	M	Temp.	Pres.	M
− 19.1	76.00	47.695	0.0	76.00	47.22	98.0	76.00	46.49
	62.22	47.42		73.80	47.19		74.37	46.48
	33.83	46.84		35.63	46.59		34.31	46.30
	19.54	46.47		18.55	46.38			
	9.76	46.365	21.5	76.00	46.94			
− 14.5	76.00	47.53		35.28	46.475			
	74.12	47.495		19.49	46.255			
	37.73	46.83		18.98	46.25			

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[1] A. Smith and Lombard, *J. Am. Chem. Soc.*, **37**, 38 (1915).

The figure shows that the isothermal M curves converge to the same value for M at $P = 0$, the value there being exactly that demanded by the theory. At all other values of the pressure P, deviations exist and, for equal values of P, they are greater the lower the temperature.

These discrepancies which are illustrated by the above example, but which are found to exist to a greater or less extent for all gases, cannot be explained on the basis of the chemical association or dissociation of the molecules. Diffusion experiments do not reveal any such influences at work as were found with ammonium chloride. Some other effect, or effects, must be the cause of these departures from the ideal gas law.

A striking example of deviation from the ideal gas laws is obtained by a study of the mixing of two gases between which no chemical reaction is known to take place. Thus, when equal volumes of two gases each at atmospheric pressure are mixed in a vessel having exactly twice the volume of either gas, the resultant pressure of the mixture is seldom found to be one atmosphere. Table VI gives the pressure changes obtained when a series of pairs of gases were mixed in this way.

TABLE VI

(Temp. 21° C., initial press. 760 mm.)

Gases	Change in press. (mm.) on mixing equal vols.	Calculated pressure change	Difference
H_2 He	0.1	0 + 0 = 0	+ 0.1
H_2 CO_2	1.1	0 + 1.1 = 1.1	0.0
H_2 $(CH_3)_2O$	3.4	0 + 3.5 = 3.5	− 0.1
He CO_2	2.0	0 + 1.1 = 1.1	+ 0.9
He $(CH_3)_2O$	4.1	0 + 3.5 = 3.5	+ 0.6
CO_2 $(CH_3)_2O$	0.3	1.1 + 3.5 = 4.6	− 4.3

Van der Waals' Equation: In 1873 van der Waals attempted to account for the deviations from the ideal gas law on theoretical grounds by taking into consideration the existence of molecular forces and the space occupied by the molecules themselves. The result of his effort is given by the equation which bears his name, and although we now know that it is only a first order correction, nevertheless this equation has been of inestimable value particularly as the second order corrections are difficult to define with mathematical exactness.

Van der Waals employed the following reasoning. In the equation

$$pv = NRT,$$

the volume v should only represent the space throughout which the molecules are free to move and should therefore be replaced by $(v - b)$ where b is proportional to the space occupied by the molecules themselves. Since the molecules which approach one another cannot have their centers within the hemisphere of radius σ, it follows that b is equal to $\frac{2}{3}\pi n\sigma^3$, where n is the total number of molecules in volume v and σ the molecular diameter. Hence, the equation becomes

$$p(v - b) = NRT.$$

Furthermore, the molecular forces will affect the pressure of the gas. A molecule in the center of the gas is surrounded on all sides by an equal number of molecules; hence, the effect of molecular attraction on the average velocity with which it moves will be zero. This will not be true of the molecules near the boundaries of the gas phase. The molecules will be attracted equally in all directions tangential to the boundary surface of the gas; perpendicular to this surface, however, the attraction towards the main body of the gas will not be compensated. Hence, the molecules moving perpendicular to the surface will have their velocity diminished by an amount proportional to the attractive force. But the pressure is registered on the manometer by these very same molecules which are moving out of the main body of the gas. The pressure P registered by the manometer is therefore smaller than the true pressure corresponding to the average velocity of the gas molecules. The gas law should therefore be written

$$(P + f)(v - b) = NRT,$$

where f represents the effect of the molecular forces. This factor f is proportional to the number of molecules colliding with the manometer and, therefore, the number of molecules in the surface layer of a gas and the effect on the surface layer will be proportional to the number of molecules in the rest of the gas. Both these quantities are proportional to the density of the gas and, hence,

$$f = k\rho^2 = \frac{a}{v^2},$$

since the volume of a given mass of gas is inversely proportional to its density.

$$\left(P + \frac{a}{v^2}\right)(v - b) = NRT \tag{41}$$

is known as van der Waals' equation.

It has already been pointed out that, at infinite dilution, the ideal gas law is found to be true. Van der Waals' equation is in agreement with this. Furthermore, the actual values found for the pressure of gas even at very high pressures are approximately represented by this equation.

The properties of gases at high pressures and low temperatures may now be discussed with van der Waals' equation as a guide. However, before so doing, the assumptions made by van der Waals will be indicated in order to show that a great degree of exactness cannot be expected from van der Waals' equation.

It was assumed that b, representative of the space occupied by the molecules, should be independent of the temperature and pressure. That this is not the case can be demonstrated by deriving the equation in an entirely different manner, which shows also how the volume of the molecules affects the pressure registered by the manometer. It is assumed for the moment that the molecular attraction can be neglected. The molecules which strike the manometer do not travel from the midst of the bulk of the gas, but come from a distance, l, where l is the mean free path. Consider a manometer surface one square centimeter in area which is in contact with a gas of volume V, and let N represent the total number of molecules and n the number of molecules per cubic centimeter. Let x be the velocity of the molecules. Then, the number of impacts recorded per second by one molecule will be $\frac{1}{2}\left(\frac{x}{l}\right)$, the expression $\frac{x}{l}$ being halved because only the impacts on the manometer and not those at the other end of the path are here considered. The number of molecules concerned will be $\frac{1}{3}n(2r + l)$, where r is the radius of the molecule, $(2r + l)$ being the distance from which the molecules can reach the manometer, the numerical factor, $\frac{1}{3}$, signifying the number which on the average move perpendicular to the manometer surface. Each impact records a pressure $2mx$, so that the pressure per square centimeter, p, is

$$p = 2mx \cdot \tfrac{1}{3}n(2r + l)\left(\frac{1}{2} \cdot \frac{x}{l}\right) \qquad \text{or} \qquad p = \tfrac{1}{3}mnx^2\left(1 + \frac{2r}{l}\right).$$

Since l is large compared to r, this may be written

$$p\left(1 - \frac{2r}{l}\right) = \tfrac{1}{3}mnx^2,$$

because

$$\left(1 + \frac{2r}{l}\right)^{-1} = 1 - \frac{2r}{l}.$$

From the definition of N and n it follows that $n = \frac{N}{V}$. Hence,

$$pV\left(1 - \frac{2r}{l}\right) = \tfrac{1}{3}mNx^2 = RT,$$

where V contains one gram molecule. But l, the mean free path, is equal to

$$\frac{1}{4\sqrt{2}\,\pi r^2 n} = \frac{1}{4\sqrt{2}\,\pi r^2} \cdot \frac{V}{N}.$$

Hence,

$$pV\left(1 - \frac{8\sqrt{2}\,\pi r^3 N}{V}\right) = RT$$

or

$$p(V - 8\sqrt{2}\,\pi r^3 N) = RT. \tag{42}$$

But, $\frac{4}{3}\pi r^3 N$ is the volume occupied by the molecules. The result is therefore obtained by means of this derivation that the volume correction is proportional to the space occupied by the molecules but the conclusion is based on a constant mean free path. It has already been shown that the mean free path will be affected by the molecular forces, the extent to which the mean free path is affected being dependent on the temperature. The lower the temperature the greater is the effect on the mean free path. Hence, b of van der Waals' equation cannot be expected to remain constant but will be proportional to some function of the absolute temperature.

Even the constancy of the space occupied by a molecule is an assumption which cannot be taken for granted. T. W. Richards[1] has drawn attention to the probable effect of temperature on the volume of the molecules. If the volume of the molecule is subject to change, it is beyond question that the magnitude of these molecular forces will also be affected, so that a will also vary with the temperature. Sufficient has been said to draw attention to further corrections to which the equation of van der Waals must be subjected. It is, however, a first order approximation and the basic idea of taking into account molecular forces and the volumes of the molecules has served the purpose of amplifying the molecular kinetic theory, making it possible to appreciate, qualitatively at least, the phenomena connected with compressed gases and liquids.

Temperature Changes on the Expansion of a Gas: In the discussion of an ideal gas which expands without performing external work, that is, expansion into a vacuum, the absence of any temperature change was made apparent. In the case of any gas which is no longer limited to the condition that p is zero, a temperature change does occur. This temperature change was discovered by Joule and Thomson and is known as the Joule-Thomson effect.[2] This effect consists in a rise or fall in temperature when a gas expands according to a mechanical arrangement illustrated by Case 2, Fig. I. This arrangement is actually attained by use of a porous plug. We may now inquire into the influence of the volume of the molecules and of the molecular forces in this effect.

(*a*) *Effect of Volume:* The space occupied by the molecules themselves accounts for a rise in temperature; the force of attraction between the molecules accounts for a drop in temperature. Each of these factors will now be considered separately and in detail.

Suppose that a gas consists of molecules having a definite volume but having no attraction for one another. In this case a in van der Waals' equation would be zero, and the equation

$$p(v - b) = NRT$$

would represent the relation between the pressure, volume, and temperature of this gas. At a fixed temperature, this equation can be written

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[1] Richards, *J. Am. Chem. Soc.*, **36**, 617 (1914).

[2] Thomson and Joule, *Phil. Trans.*, **143**, 357 (1852).

$$pv = k + bp.$$

This means that the value for pv increases with rise in pressure. Since pv is a measure of the mechanical energy which may be derived from a gas, it follows that, when a gas expands without doing external work, a certain amount of available energy has been lost equivalent to $b \cdot dp$, where dp is the change in pressure. Since this is impossible, it follows that the gas must have been heated upon expansion. Thus, from thermodynamic considerations the volume effect of the molecules will cause every gas to warm up on expansion.

In order to obtain a mental picture of the volume effect of the molecules it is convenient to write van der Waals' equation in the form derived in the previous section, namely,

$$pv\left(1 - \frac{2r}{l}\right) = k$$

at a fixed temperature. Since the mean free path l is inversely proportional to the number of collisions between the molecules, this may be written

$$pv(1 - k'n_c) = k,$$

where n_c is the number of collisions per second. It is now only necessary to realize that a gas must contain potential energy due to the impacts of its molecules. When two molecules collide, the impact I is equal to the product of the restoring force F, multiplied by the time during which it acts, dt, that is, the time during which the molecules are in actual contact. A time of contact equivalent to zero would require infinite rigidity (an infinite force), which is impossible. The impact I will, under all circumstances, have a definite value, and hence, the time of contact, dt, will have a definite value. During this time of contact the kinetic energy of the molecules will exist largely in the form of potential energy, say by a distortion of the shape of the molecule. The amount of potential energy which a gas has will therefore be proportional to n_c, the number of collisions which occur. Since the expansion of a gas means a decrease in the number of collisions and hence a decrease in the potential energy, a corresponding increase in kinetic energy will occur, that is, the gas will warm up.

When a gas is highly compressed so that the value of l diminishes until it is commensurable with r, the radius of the molecule, the higher terms of the expansion

$$\left(1 - \frac{2r}{l}\right)^{-1} = 1 - \frac{2r}{l} + \frac{4r^2}{l^2} - \cdots$$

have to be taken into account, and, when $2r$ finally equals l and the value of V is that of the molecules themselves, marked deformation of the molecular form occurs with a corresponding marked increase in potential energy. Since the compressibility of a molecule varies from gas to gas, the steepness of the curvature of the latter portion of a pv curve will vary and will be a function of the compressibility. Curve 1, Fig. 9, represents the relation between the product pv and the pressure of a gas in which only the space occupied by the molecules is taken into account. The first portion of the curve is a straight line represented by the equation

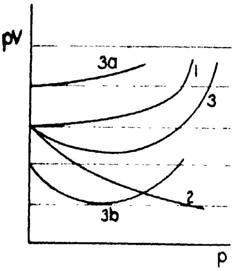

Fig. 9

$$pv = k + bp.$$

The second portion of the curve takes into account the large potential energy due to the actual deformation of the molecules which occurs when their volume approaches that of the containing vessel.

(*b*) *Molecular Force Effect:* Suppose that a gas consists of molecules which are attracted to one another with forces so large that the effect of the space occupied by the molecules can be neglected in comparison therewith; the equation

$$pv = k - \frac{a}{v}$$

will represent the relation between pressure, volume, and temperature of such a gas. Curve 2, Fig. 9, gives the relation between pv and p. It is seen that the product pv decreases with the pressure. The gas has, therefore, a smaller amount of available energy at a higher pressure. When it expands without performing external work, the gas gains available energy, and this can only be done at the expense of its own intrinsic energy; that is, the gas will cool down. It is not very difficult to visualize the mechanism on which this cooling depends. Expansion of the gas means that the average distance between the molecules is increased. Since this necessitates a movement of the molecules against their force of mutual attraction in order to attain the new position, this movement is only accomplished at the expense of their kinetic energy. In other words the gas cools down upon expansion.

(*c*) *Combined Effects of Volume and Molecular Forces:* Curve 3, Fig. 9, represents the actual relation between pv and p as given by van der Waals' equation. The first part of Curve 3 will approximate to either Curve 1, or Curve 2, according to whether the volume effect b, or the molecular force effect a, predominates. Since, in all gases, the space occupied by the molecules is appreciable and of the same order of magnitude, whereas this cannot be said of the relative magnitudes of the molecular forces of various gases, it follows that the volume effect is bound to predominate at the higher pressures.

Temperature plays a large part in determining to which curve the actual pv curve of a gas will approximate. At higher temperatures, Curve 3 approaches Curve 1; at low temperatures it approaches Curve 2 at the lower pressures. This is due to the relatively greater influence which the molecular forces have on slower moving molecules. Thus Curves 3*a*, 3, and 3*b* represent isothermal pv, p curves for the same gas at a high, an intermediate, and at a low temperature respectively. Thus, to take actual examples,[1] these temperatures are, for hydrogen, 0°, − 150°, and − 210°. For nitrogen the temperatures in question are 200°, 0°, and − 150°. For carbon dioxide, they are 500°, 20°, and − 20°. This means that, for these gases, the molecular force of mutual attraction of hydrogen is very small, whereas for carbon dioxide it is relatively large, and for nitrogen it is intermediate in magnitude.

In the liquefaction of gases the cumulative Joule-Thomson effect is employed. Since the change in temperature Δt for a gram molecule of gas on expanding can be approximated by the equation

$$\frac{p_1v_1 - p_2v_2}{C_v} = \Delta t, \tag{43}$$

it is seen that, from the practical point of view, the determination of the pv, p curve is of considerable importance. The original temperature of the gas must correspond to a temperature where the form of the $pv - p$ curve is given by Curve 3, Fig. IX. Obviously, this varies from gas to gas. It also follows from the above equation that the temperature lowering on expansion increases in magnitude the lower the original temperature. Again, the pressure of the gas before expanding has an optimum value from the point of view of efficiency given by the minimum value for pv in the pv, p curve.

(*d*) *Miscellaneous Temperature Changes.* When a gas expands in the manner depicted by Case 2, Fig. 1, the temperature changes of the gas as a whole are given by the preceding equation. This change in temperature corresponds to complete equilibrium after expansion. During the actual expansion relative temperature changes may well take place in various parts of the expanding gas. The persistence of direction has been mentioned in connection with the correction for the mean free path.

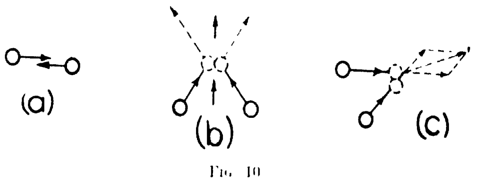

Fig. 10

In Fig. 10 various types of collisions between molecules are shown where for purposes of simplicity their shapes are taken as spheres. In a collision between molecules whose directions of motion are parallel, Case (*a*), Fig. 10, any direction after collision is equally probable. Where the motion of the two molecules is not along parallel lines, Case (*b*), Fig. 10, the average direction of the two is favored by the velocity component which they have in common.

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[1] Amagat, *Ann. Chim. Phys.*, (5) 19, 345 (1880).

It is due to this persistence in direction that, after expansion, equilibrium in pressure throughout the vessel takes place so rapidly. Just after the diaphragm, Case 2, Fig. I, has been removed, there will be a larger number of molecules per unit volume in the original volume than in the newly added volume of the containing vessel. Hence, the chance for a collision where the velocity will persist in the direction from dense to less dense is much greater, with the result that pressure is very rapidly equalized. Now, during this period, collisions, of which type c is an extreme case, are frequent. In any collision, the velocity components of the colliding molecules resolved in a direction passing through their centers are interchanged, whereas the original velocity components at right angles persist. Hence, in this extreme case, if the original velocities of the two molecules were each x before collision, after collision one molecule would be at rest and the other would be moving with a velocity $\sqrt{2}\,x$, in a direction from dense to less dense. The temperature of the gas in the newly added volume of the containing vessel will therefore be momentarily somewhat higher relative to that of the gas in the original volume. If in Case 2, Fig. I, the two portions of the vessel are brought into communication with one another through a small opening, the gas going through may be looked upon as behaving like a piston, with the result that the temperature difference between the two volumes may be quite marked, especially as the chance for temperature equilibrium to be quickly established is greatly reduced. If, however, the temperature is averaged in both compartments, this average temperature differs from the original temperature by the amount

$$\frac{p_1v_1 - p_2v_2}{C_v}.$$

In the isothermal expansion of a gas where work is obtained, Case 1, Fig. I, it has been shown that this work is equal to $\int_{v_1}^{v_2} pdv$ per mol, in the case of an ideal gas. From what has preceded it follows that, to this expression for the work done, the quantity $p_1v_1 - p_2v_2$ must be added in order to obtain the total energy change involved.

Gas Mixtures: That the pressure of a gas mixture is equal to the sum of the partial pressures of the gases composing the mixture is known as Dalton's law.[1] If the gases are ideal gases, the validity of this law is apparent from the derivation of the ideal gas law, which gives

$$p_1v = \tfrac{1}{3}m_1n_1x_1^2,$$
$$p_2v = \tfrac{1}{3}m_2n_2x_2^2,$$
$$Pv = \tfrac{1}{3}m_1n_1x_1^2 + \tfrac{1}{3}m_2n_2x_2^2,$$

and hence

$$P = p_1 + p_2,$$

where m_1, m_2 are the weights; n_1, n_2 the numbers; and x_1, x_2 the velocities of the molecules of the two gases; p_1, p_2 are the pressures exerted when each of the gases separately occupies the volume, *v*, and *P* is the pressure exerted when both occupy this volume at the same time.

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[1] Dalton, *Nicholson's J.*, **5**, 241 (1801).

When one liter of a gas, *A*, and one liter of a gas, *B*, each at a pressure of one atmosphere, and at 24° C., are brought into a two-liter vessel, there may be a considerable change in pressure, as is illustrated by the results given in Table VI. This is to be expected from the discussion in the preceding sections. Thus, when one liter of methyl ether at a pressure of 760 mm and a temperature of 24° C. is placed in a two-liter vessel, the pressure is found to be 383.5 mm., not 380 mm. Hydrogen gas, on the other hand, is so nearly ideal that doubling its volume just halves its pressure. Column 3 in Table VI gives the pressure change of the gas mixture, calculated on the basis of Dalton's law, assuming that the gases do not influence one another but taking into account the aberrations from the ideal gas law for each individually. Column 4 gives the difference between the pressures calculated in this way and those found experimentally, showing that the gases do exert an influence upon one another in some cases.

The mutual influence which two different species of gas molecules can have upon one another can best be discussed by means of the data in Table VI. Under the conditions of temperature and pressure of the experiment hydrogen and helium are so nearly perfect gases that they obey Boyle's law. Hence, on mixing them, there is no pressure change, showing, as would be expected, that they have a negligible attraction for one another. Hydrogen and methyl ether and hydrogen and carbon dioxide show an increase in pressure corresponding nearly to the calculated pressure change. This may be taken as an indication that they do not influence one another since they register a pressure which is the sum of the partial pressures when each occupies the volume alone.

However, that there is a slight attraction follows from a consideration of the results obtained when helium and carbon dioxide and helium and methyl ether are mixed. In both cases there is a pressure registered greater than the calculated pressure. The explanation is easily found. If the carbon dioxide is allowed to expand from a volume of one liter to a volume of two liters, the pressure changes from 760 mm. to 381.1 mm. but even at this low pressure the carbon dioxide is far from being a perfect gas. If the attraction between the molecules of carbon dioxide were to cease, the pressure in the two-liter volume would be greater than 381.1 mm. The attraction between the molecules comes into play to the greatest extent at the moment of collision; the presence of the helium reduces the number of collisions between carbon dioxide molecules, with the result that the effective attraction between the carbon dioxide molecules is lowered. The carbon dioxide becomes more nearly a perfect gas, with a resulting increase in pressure. The same is true of the mixture of methyl ether and helium. On account of the great difference in the size of the methyl ether and helium molecules, however, the number of collisions between methyl ether molecules is not reduced to the same extent and, consequently, the percentage effect is not so large.

In the case of the carbon dioxide-methyl ether mixture, the magnitude of the negative value in the difference column of Table VI shows that there is a considerable attraction between methyl ether and carbon dioxide molecules which is nearly the same as the attraction of each species for itself.

In a two-component gas mixture there are three forces of attraction which come into play, two between the same species of molecules and one between the different species. The total gas pressure will depend on the magnitude of these attractions and also on the extent to which these attractions can come into play. The latter depends on the relative volumes and numbers of molecules which govern the number of collisions.

The pressures of gaseous mixtures at high pressures have been examined by Masson and Dolley[1] and some of the results obtained for argon-ethylene mixtures are given in Table VII.

TABLE VII

PRESSURES OF ARGON-ETHYLENE MIXTURES

Pressure Calculated (Atmospheres)	Difference between Pressure Observed and Pressure Calculated (Atmospheres)		
	24.74 per cent	49.95 per cent	90.06 per cent
30	− 0.75	− 0.85	− 0.45
50	− 1.7	− 2.7	− 1.2
70	− 3.35	− 5.45	− 1.95
80	− 4.3	− 6.8	− 0.75
90	− 5.2	− 7.65	1.0
100	− 6.05	− 8.0	3.0
110	− 6.60	− 8.15	5.25

The first column gives the pressure calculated by adding the pressures which each component would exert if it occupied the volume alone. The other columns give the difference between the observed results and those calculated in this way. At the head of each of these columns the molecular percentage of the ethylene in the ethylene-argon mixture is given.

The conclusions drawn by Masson and Dolley are that the space available for each constituent is partly blocked by the molecules of the other, the effect being that symbolized by van der Waals' *b*. This effect predominates in the ethylene-rich argon mixture, so that the pressure exerted by the mixture is greater than the sum of those of the constituents taken separately. At lower pressures and in the case of mixtures less rich in ethylene, the attraction between the molecules outweighs the *b* effect.

Masson and Dolley have shown that ethylene-oxygen mixtures exhibit practically the same pressure changes as do argon-ethylene mixtures, while oxygen-argon mixtures exert pressures much closer to those calculated. The *pv*-*p* curves for various concentrations of ethylene and argon show a continuous change from the *pv*-*p* curve of one constituent to that of the other.

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[1] *Proc. Roy. Soc.*, **103 A**, 524 (1923).

CHAPTER IV

THE LIQUID STATE OF AGGREGRATION

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A discussion of the liquid state of aggregation may profitably be introduced by a consideration of critical phenomena and the factors governing the liquefaction of gases. Increase in pressure and lowering of temperature will cause a gas to liquefy. Of these two factors experience has shown that the latter is by far the more important. For each gas there exists a definite temperature above which it is impossible to liquefy the gas no matter what pressure may be applied. This temperature is known as the critical temperature. It is dependent on the molecular forces of attraction. These molecular forces vary as the inverse power of the distance between the molecules and, as will be seen later, this power is considerably greater than 4. The force may therefore be very considerable when the molecules are in close proximity, but it diminishes rapidly, so that, beyond a certain distance, it may be looked upon as being quite negligible. The force is probably chemical in nature depending on the motions and relative distribution of electrons and nuclei in the molecules.

If a collision takes place between two molecules each moving with a velocity x, the kinetic energy of each, after collision, will be $\frac{1}{2}mx^2$. In moving out of the field of force set up during the collision the work done by each is $\int_0^s fds$, where s is the effective range of the molecular force. If $\int_0^s fds$ is greater than $\frac{1}{2}mx^2$, it follows that, before traversing the distance s, their velocity will have been reduced to zero. Consequently, they will now attract each other and the potential energy will be changed into kinetic energy. The result will be that, at the moment of collision, their velocities will again be x. These two molecules consequently will form an oscillating system whose parts will never separate a distance further than s. If another molecule is added to this system, the three will form a similar system which is held together more firmly because the three molecules will be attracting each other mutually. At this point it must be emphasized however, that, on the supposition that the force falls off so rapidly with the distance that the effective range is small, the addition of further molecules beyond a certain number does not have a cumulative effect. Consequently, when the temperature of a gas is reduced just below the value given by $\frac{1}{2}mx^2 = \int_0^s fds$, all the molecules of the gas will form a system which will no longer uniformly fill the containing vessel, but will occupy a definite space independent of this volume of the vessel. In a gas in which all the molecules moved with the same velocity, this would be the temperature at which liquefaction would take place, i.e., the critical temperature. The conglomerated molecules, that is, the liquid, would then comprise all the molecules originally in the containing vessel giving a liquid having no vapor pressure. But, the velocities of the molecules in a gas vary enormously, as indicated by Maxwell's distribution law. Therefore, the critical temperature has to be defined as the temperature at which the average kinetic energy of the molecules is such that $\frac{1}{2}mx^2$ is equal to $\int_0^{s} fds$. Although a conglomeration of molecules is only possible below this critical temperature, this liquefaction will not necessarily occur. The prevailing pressure will be a factor. In no case will all the molecules conglomerate at the critical temperature because there will always be some whose kinetic energy is greater than the average.

Suppose a gas exists at a temperature slightly below the critical temperature. The conditions under which liquefaction will occur merit consideration. If one assumes that, in a small region, the conglomeration of molecules has taken place, that is, a small region exists in which the gas may be said to be liquid, the molecules in this liquid will have velocities which will also vary in accordance with Maxwell's distribution law. The molecules whose velocity is greater than the critical will be continuously escaping so that the amount of liquid will be correspondingly diminishing. On the other hand, the molecules from the surrounding gas are continuously entering and forming part of the liquid. Whether this region of liquid will increase or decrease will depend upon which of the two processes predominates. This in turn will depend on the relative concentrations of the molecules in the gas and in the liquid. Since the concentration of the gas is dependent on the pressure, it is obviously possible to increase the concentration of the gas by increasing the pressure to that at which the liquid region can exist. Thus, at the critical temperature the pressure which is just necessary to produce liquefaction is called the critical pressure. The pressures necessary to cause liquefaction at temperatures below the critical temperature are called the vapor pressures of the liquid.

It is instructive to follow the changes which take place in the equilibrium between a liquid and its vapor with rise in temperature. The liquid consists of molecules moving with various velocities, the average being given by the gas law relation, $RT = \frac{1}{3}mnx^2$. Those molecules which are a considerable distance below the interface are attracted on the average equally in all directions. A molecule moving towards the boundary of the liquid will gradually come into a field of force in the direction of the main body of the liquid. This field of force will be proportional to $\Delta - \rho$, where Δ is the density of the liquid and ρ that of the vapor. A molecule will therefore have a better chance of escaping from the gas to the liquid than from the liquid to the gas. It follows that every gas molecule moving towards the liquid surface will enter the liquid, but those molecules of the liquid whose velocity is such that $\int_0^{s} f(\Delta - \rho)ds$

is greater than $\frac{1}{2}mx^2$ will not be able to enter the gas even if they are moving in the proper direction. This may be shown experimentally by removing the vapor above a liquid, whereupon the liquid cools down; only those molecules with a velocity greater than that given by the above equation can escape, that is, the average kinetic energy of the molecules remaining in the liquid is reduced; its temperature therefore falls. This is, of course, the latent heat of evaporation. If the space above the liquid is enclosed, the escaping molecules will accumulate in this space and will eventually return to the boundary of the liquid in such numbers that equilibrium will result. At equilibrium the number of molecules leaving the liquid is therefore exactly equal to the number returning from the vapor above. At equilibrium no further temperature changes occur; it is true that the fast moving liquid molecules entering the vapor reduce the average velocity of those remaining, but the vapor molecules which return have their velocity component perpendicular to the surface of the liquid increased by the field of force, so that the molecules which are retained also have a velocity above the average. The vapor pressure of a liquid is therefore due to a dynamic equilibrium which results when the number of molecules leaving the liquid is just equal to the number returning from the vapor above. The term vapor is applied to a gas at a temperature below the critical temperature, the field of force existing at the boundary of liquid and vapor is known as the surface tension.

The effect of rise in temperature on the vapor pressure of a liquid may now be examined. A rise in temperature means an increased kinetic energy of the molecules of the liquid so that a larger number than before will have a velocity which will carry them through the boundary against the force of surface tension. Hence, a larger number will escape with the resultant increase in the vapor pressure. Furthermore, the increased kinetic energy will cause an expansion of the volume occupied by the liquid proper, since, from the boundary inwards, the greater kinetic energy of the molecules will enable them to move further apart before the molecular forces cause their return. Hence, Δ decreases, whereas p increases, the surface tension decreases. A rise in temperature has a cumulative effect on the vapor pressure increase since not only a greater number of molecules have velocities sufficiently great to carry them out of the field of molecular attraction, but also the field of attraction has been considerably diminished. The vapor pressure will therefore increase according to some function of the temperature where the temperature variable is a higher power than one.

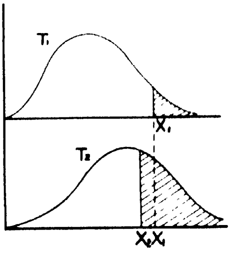

Fig. 1

The relationship between temperature and vapor pressure can be brought out by drawing curves representing the distribution of velocities as given by Maxwell's distribution law, the equation for which was developed in Chapter

III. In Curve T_1, Fig. 1, the ordinates are proportional to the number of molecules having velocities given by the abcissa. If x_1 represents the minimum velocity necessary for a molecule to escape from the liquid, the shaded area represents the proportion of the molecules which have a chance to escape. Curve T_2, representing the velocity distribution at a higher temperature, shows the manner in which this shaded area increases, especially as the critical velocity x_2 at the higher temperature has been diminished as well.

With a continued rise in temperature, Δ will eventually coincide with ρ, so that the surface tension will be zero, the temperature at which this occurs being the critical temperature. Observation has shown that, when a gas, under its critical pressure and slightly above its critical temperature, is gradually cooled, a cloud appears just before the formation of the liquid layer. Above the critical temperature, the average kinetic energy of the molecules is greater than $\int_0^s fds$, the range of molecular force being confined to the surface layer of the gas. Liquefaction might be expected to take place from the surface. The appearance of the cloud is due to fluctuations in the density of the gas. A chance movement of the molecules will doubtless cause a variation in density provided that a small enough region is considered, and, hence, liquefaction may start from some such small region of greater density. Above the critical temperature, the average kinetic energy of the molecules is such that the majority have a chance to escape from a liquid region. Below the critical temperature the average kinetic energy of the molecules is such that the chance to escape from the liquid region is less than unity, so that if the pressure is high enough liquefaction will occur. At this point, it may be indicated that, on the above interpretation, the critical temperature on the absolute scale is a measure of the forces of attraction; other properties, therefore, such as surface tension and latent heat of evaporation, which are dependent on molecular forces, are related to the critical temperature.

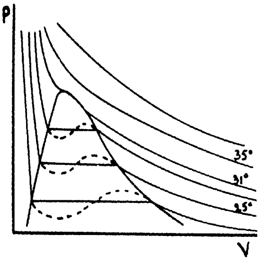

FIG. 2. P-V Diagram for Carbon Dioxide

Isothermal *P*-*V* Curves: The relation between the pressure and volume of carbon dioxide at high pressures and over a range of temperature including the critical has been determined experimentally by Andrews.[1] The experimental values gave isothermal p-v curves which closely resembled those given by van der Waals' equation. In Fig. 2 a series of these curves deduced from the results of Andrews are shown. At the highest temperatures the curves most closely resemble the rectangular hyperbola demanded by the mathematical expression of Boyle's law; at a temperature slightly above the critical temperature an inflexion occurs, which, more pronounced at the critical

[1] *Trans. Roy. Soc.*, **159**, 583 (1869).

temperature (31.1°) itself, becomes a discontinuity at temperatures below the critical. The first portion of the 25° isothermal, for instance, shows the pressure-volume relationship of carbon dioxide in the liquid state. The break corresponds to the vapor pressure of the liquid at that temperature where an increase in volume will not be accompanied by a pressure change until no liquid is left. The rest of the curve denotes the p-v relationships of carbon dioxide in the gaseous state. The higher the temperature the greater the vapor pressure of the liquid, and therefore the shorter the portion of the curve which corresponds to a change from liquid to gas until, at the critical temperature, this portion of the curve shrinks to a point. The change from liquid to gas which experimentally gives a straight line is not followed by the curve given by van der Waals' equation,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

The latter gives the dotted line shown in the case of the 25° isothermal.

Considerable controversy has been aroused over the interpretation of the theoretical, van der Waals' curve in the region of coexistence of gas and liquid. It has been suggested that the first portion represents the relation between the pressure and volume of the liquid above its point of ebullition, and the second portion that of the vapor compressed beyond the liquefaction point without condensation. This may be so for the very first portions of each of the dotted curves, but it is obviously absurd to go beyond this. It may be pointed out that the average value for the pressure ordinates is the same for both experimental and theoretical curves, that is,

$$\int_{v_1}^{v_2} p\,dv = p_0(v_2 - v_1),$$

where v_2 and v_1 are the volumes of vapor and liquid respectively, and p_0 is the vapor pressure. The failure of van der Waals' equation to agree with that portion of the curve where evaporation takes place is due to the existence of two phases, whereas van der Waals' deductions are based on the existence of only one. When the liquid and vapor are in equilibrium, the volume, pressure, temperature, and number of gram molecules of each, separately substituted in the equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = NRT,$$

gives the correct values for a and b. It is equivalent to using two sets of units in one equation to attempt to apply van der Waals' equation to the two phases at once. That it holds for each phase separately is brought out in a striking way by the calculated relations between a and b and the critical temperature and pressure.

It will be noticed that van der Waals' equation is cubic as regards the variable v, viz.,

$$v^3 - \left(b + \frac{RT}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0.$$

One of the roots of this equation is always real; the other two may be real or imaginary. It will be noticed that in the isothermals below the critical temperature there are three real values for v, given by the theoretical curve corresponding with the vapor pressure of the liquid. The higher the vapor pressure the closer together are the three values for v, until at the critical temperature where, in the presence of a solitary phase, the theoretical and experimental curves again coincide, the three values for v are identical. Hence, on substituting the critical pressure p_c, and the critical temperature T_c, v_c, the critical volume, will give an identical equation $(v - v_c)^3 = 0$. On expanding this equation and equating the coefficients of the various powers of v in the above equations, three equations are obtained giving a relation between the critical constants and a and b:

$$v_c = 3b; \qquad p_c = \frac{a}{27b^2}; \qquad T_c = \frac{8a}{27bR}.$$

The experimental values of a and b, obtained from Andrews' data for carbon dioxide, were used to calculate the critical temperature and pressure giving values which were within twenty per cent of these latter constants determined experimentally. This agreement is evidence of the truth of the fundamental ideas involved in the equation of van der Waals. From what has been said in a previous section exact agreement can hardly be expected. It is greatly to be regretted that so little reliable experimental evidence is available whereby the above relationship can be further examined.

From the data of a few substances for which a and b have been accurately determined, it seems that $v_c = 4b$ is in better agreement with the facts than the expression $v_c = 3b$ given by van der Waals' equation. Furthermore, $v_c p_c$ is equal to $0.375RT_c$ from the above equations, whereas the experimental results are in agreement with $p_c v_c$ equal to $0.27RT_c$. These experimental results have been incorporated in innumerable empirical relationships involving p, v, and T. These equations, with one or two exceptions, have lost their theoretical significance and have done little to further the development of the kinetic theory.

To van der Waals is given the credit for the origin of the term "continuity of state" as applied to the gaseous and liquid states. The significance of this term is brought out by the two isothermals, one at a temperature just slightly above the critical, the other just slightly below. The curvature of these two isothermals is exactly the same at all points although the first represents solely the substance in the gaseous, the other the substance in both gaseous and liquid states. The parallelism of these two isothermals is experimentally proven.

Other Equations of State: Clausius[1] showed that the results obtained by Amagat for the relation between pressure and volume at very high pressures could be best represented by modifying van der Waals' equation, thus:

$$\left\{ p + \frac{a_1}{T(v + c)^2} \right\} (v - b) = RT.$$

This equation does not satisfactorily represent the pressure-volume relations for carbonic acid and ethylene[2] D Berthelot[3] has made use of this equation for the representation of the pressure-volume relationship of a gas at low pressures by putting c equal to zero in the Clausius equation. By making use of the premise that the equation is to be applied at low pressures, and thus making it possible to neglect second order magnitudes, and boldly replacing numerical coefficients by those which corresponded to experimental results, for example, putting R equal to $\frac{32}{9} \frac{v_c p_c}{T_c}$ instead of the theoretical R equal to $\frac{8}{3} \frac{v_c p_c}{T_c}$, Berthelot derived the equation

$$pv = RT \left\{ 1 + \frac{9}{128} \frac{pT_c}{p_c T} \left(1 - 6 \frac{T_c^2}{T^2} \right) \right\} .$$

This equation has been of great value in extrapolating the density of a gas to low pressures and has been used by Guye[4] for the actual calculation of the atomic weights from the measurements of gas density.

An equation of state suggested by Dieterici,[5] viz.,

$$p = \frac{RT}{(v - b)} e^{-\frac{a}{RTv}},$$

has the merit of giving $p_c v_c$ equal to $0.27 RT_c$ which, as was pointed out in the previous section, is in better agreement with the experimental facts than the similar deduction from van der Waals' equation. Applied to the experimental data of Young[6] on isopentane, Dieterici's equation is in good agreement except at higher pressures

An equation of state which represents the experimental facts with greater exactness than those previously given is that of Keyes[7] which is based on the following theoretical considerations. The molecules are supposed to consist of electrons moving in orbits according to the Bohr model of the atom The electrons and positive nuclei of any two molecules attract and repel one another according to the inverse square law, and, as the average distance between the electric charges will be equal, the attractions and repulsions between the positive and negative charges mutually cancel. The magnetic field due to the revolving electrons does not cancel, giving rise to magnetic doublets which attract each other according to the inverse fourth power. This would give van der Waals' equation as far as the term $\frac{a}{v^2}$ is concerned. Keyes makes the statement that the above structure of the atom does not give exactly an inverse fourth power law but that the attraction increases slightly more rapidly than the inverse fourth power. This would lead to a modified form of van der Waals' equation,

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[1] *Wied. Ann.*, **9**, 337 (1880)

[2] Sarraw, *Compt rend*, **94**, 845 (1882)

[3] D. Berthelot, Sur les Thermomètres à Gaz, 1903

[4] Guye, *J. chim. phys.*, **6**, 769 (1908).

[5] *Wied. Ann.*, **65**, 826 (1898).

[6] Young, *Sci. Proc. Roy. Dublin Soc.*, **15**, 126 (1916)

[7] Keyes, *Proc Nat. Acad Sci*, **3**, 323 (1917).

$$\left\{ p + \frac{a}{(v + l)^2} \right\} (V - \delta) = RT.$$

Furthermore, instead of having δ constant, Keyes suggests that it is a function of the volume given by the expression $\delta = \beta e^{-(\alpha/v)}$.

Space Occupied by the Molecules: The critical volume, according to van der Waals, is equal to $3b$. He has shown, however, that the b of his equation is equal to four times the actual volume of the molecules. Just what is meant by the space occupied by the molecules is a highly controversial subject. In the kinetic theory, this space is taken as a sphere of radius r, where $2r$ is the distance between the centers of two molecules at the moment of collision. T. W. Richards[1] has shown that this space can be diminished by the application of large external pressures. His hypothesis of the compressible atom can be used to interpret many phenomena such as the relation between the volume of the molecule and the chemical forces between the atoms. Richards has pointed out that the compressibility of the atom will lead to a variation of b in van der Waals' equation since b is proportional to this space. With increased pressure and increased temperature one might consequently expect a diminution in b. The difficulty of testing this experimentally is due to the necessity of assuming a constant value for a in this test. Assuming a constant, b does decrease at very high pressures, and, in the case of the monatomic gas, helium, it decreases with rise in temperature. The reverse is, however, true for polyatomic gases. Richards explains this by the increased rotation at the higher temperatures driving the atoms in the molecules a little farther apart.

The fraction of the space which is occupied by the molecules in a liquid is, in spite of its importance, one concerning which a great difference of opinion exists. In Table I the space occupied by one gram molecule is given as calculated by various methods.

The first column gives the values based on van der Waals' deduction that $\frac{1}{4}b$ gives a measure of this volume. The second column gives the volume calculated from the molecular radius given by the mean free path, $l = \frac{1}{4\sqrt{2}\,\pi n_1 r^2}$, where n_1 is 2.75×10^{19} molecules per cc., and the volume of a gram molecule

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[1] *J. Am. Chem. Soc.*, **36**, 2417 (1914).

TABLE I

VOLUMES OF MOLECULES

	Volume from b $v = 4b$	Volume from Viscosity and Conductivity	Volume of Liquid at Boiling Point
H_2	5.4	6.1	30.0
He	2.4	3.4	33.0
N_2	14.3	17.4	32.0
O_2	12.8	15.3	30.0
Ar.	13.0	15.3	22.0
CO_2	12.8	28.0	30.0

is $6.06 \times 10^{23} \times \frac{4}{3}\pi r^3$. The last column gives the volume of a gram molecule in the liquid state at the boiling point. The fraction of the space occupied at the boiling point is approximately one third for most liquids. These calculations, apart from the assumptions already pointed out with regard to the effect of the molecular forces on the mean free path, are based on incompressible atoms and therefore cannot be strictly correct.

Richards has suggested that, at the critical volume, the molecules are actually touching and that further contraction with increased pressure and lower temperature is at the expense of the volume of the compressible molecule. This implies that the molecules of a gas at densities greater than the critical density, and therefore also the molecules of a liquid, are not held apart by the kinetic energy of their movement. The evidence quoted in favor of this is the small contraction of a substance which takes place when it is in the liquid, and, later on, in the solid state, at temperatures approaching the absolute zero, where the kinetic energy ceases and the molecules will be closest together.

Putting $T = 0$, the volume at the absolute zero is given by $v = b$, so that the molecules would not be touching even at that temperature if b is four times the volume. This is certainly a decided discrepancy in van der Waals' theory. Opposed to the idea of close packing in a liquid is the fluidity of a liquid and the phenomenon of diffusion, which is of such a magnitude that it points to a mean free path of the molecule commensurable at least to its diameter. It is certain that in a liquid the space occupied by the molecules is a large fraction of the total volume. This space, more correctly called the collision space, is compressible and as yet cannot be evaluated with any degree of accuracy.

Enough has been said to show the futility of applying the equation

$$\left(p + \frac{a}{v^2}\right) = \frac{RT}{(v - b)}$$

to represent exactly the pressure volume relationship of a liquid at low temperatures. If one does so, p represents the vapor pressure, and $\frac{a}{v^2}$ the cohesion of the liquid, the sum of the two being denoted as the intrinsic pressure. The term $\frac{a}{v^2}$ has been used in this way, but as yet there is no experimental **means of** determining the cohesive force and the correctness of the calculated **values,** which attain to hundreds of atmospheres. Reynolds,[1] it is true, has shown that a tube filled with a liquid free from dissolved gases can be placed on a rotating table and whirled around at such a rate that the centrifugal force corresponds to a negative pressure of twenty atmospheres before the liquid "breaks." This "break" may occur at the walls of the containing vessel or result from some gas bubble so that these measurements cannot give any quantitative values, but at least they are physical evidence of the existence of these cohesive forces represented by $\frac{a}{v^2}$.

The Equation of Corresponding States: In spite of what has been said, a deduction known as the equation of corresponding states can be made from van der Waals' equation which gives an insight into the properties of liquids. The constants a and b vary in magnitude from gas to gas so that the universal nature of the ideal gas law is lost. Since there are only these two constants, the isothermals of any two gases can be made to coincide by a variation of these two quantities. In the preceding section it was shown that the critical pressure, volume, and temperature could be represented in terms of a, b, and R. Conversely, a, b, and R can be expressed in terms of the critical constants, viz.,

$$a = 3p_c v_c^2, \qquad b = \frac{v_c}{3}, \qquad R = \frac{8}{3}\frac{p_c v_c}{T_c}.$$

Substituting the above values in van der Waals' equation and dividing by $3p_c v_c$, an equation is obtained,

$$\left(\frac{p}{p_c} + \frac{3v_c^2}{v^2}\right)\left(\frac{3v}{v_c} - 1\right) = 8\frac{T}{T_c},$$

which may be written

$$\left(P + \frac{3}{V^2}\right)(3V - 1) = 8T',$$

where

$$P = \frac{p}{p_c}; \qquad V = \frac{v}{v_c}; \qquad T' = \frac{T}{T_c}.$$

This equation is known as the equation of corresponding states. All constants characteristic of the substance have apparently disappeared. But, in order that this may be so, new scales are used for representing the pressure, volume and temperature, these quantities now being expressed in fractions of their values at the critical temperature. It follows that, if any two substances have any two of the above variables coinciding, the third must also coincide. Thus, if V_1 and V_2 are the corresponding volumes of any two substances at the corresponding temperatures T_1' and T_2', and pressures P_1 and P_2, it follows that

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[1] O. Reynolds, Collected Works, Dixon and Joly, *Phil. Trans.*, **185**, 568 (1895).

$$\frac{V_1 - V_2}{V_1} \doteq \frac{f(P_1T_1') - f(P_2T_2')}{f(P_1T_1')}.$$

Furthermore, $\frac{V_1 - V_2}{V_1}$ is equal to a constant independent of the substance, and since this is equal to $\frac{v_1 - v_2}{v_1}$, it follows that the relative change in volume for a liquid between two corresponding temperatures is the same for all liquids. This has been abundantly tested and found to be true over wide limits. It means that, if the density-temperature curve is known for one liquid and the critical temperature and the density is known for another liquid, the density of the latter liquid can be calculated at any other temperature. For this to be strictly correct, the measurements should be made not only at corresponding temperatures but under corresponding pressures as well. Since, however, the volume of a liquid is only slightly affected by the pressure, the latter condition can be neglected without causing serious error, except at high temperatures where the pressures are large.

An important result of the above theorem is that it makes it possible to measure the relative volumes of the molecules themselves by comparing the molecular volumes of liquids measured at corresponding temperatures. By comparing the values of b for various substances one would compare the spaces occupied by the molecules. Very few such values have been determined on account of the experimental difficulties involved. The critical volume, v_c, is proportional to b, and it has been shown that the volume of a liquid at the corresponding temperature is proportional to v_c. Therefore, the molecular volumes of liquids at corresponding temperatures are proportional to the spaces occupied by the molecules themselves. It happens that the boiling points of most liquids are, at the same corresponding temperature, approximately 0.62 on the corresponding temperature scale. A large amount of data has been collected[1] and its systematization has been confirmed by the above deductions. The space occupied by the molecules has been found with great consistency to be a function of the component atoms, being additive as regards their number, type, and method of linkage to neighboring atoms.

It may be pointed out that the principle involved in the equation of corresponding states does not depend on the exact form of van der Waals' equation, but that other equations of state in which the characteristic constants can be connected with the critical constants may lead to an equation in which no characteristic constants will appear when the volume, pressure, and temperature are measured on the corresponding temperature scale.

Vapor Pressure: Reference has been made in a preceding section to the qualitative dependence of vapor pressure upon temperature. Van der Waals' equation, which applies only to a single phase, does not, by itself, give any

[1] Guldberg, *Z. physik. Chem.*, **5**, 374 (1890).

indication of the magnitude of the vapor pressure at a given temperature. It is possible with the aid of thermodynamic considerations to link up vapor pressure with the latent heat of evaporation, the origin of which has also been discussed. If l represents the heat required to evaporate one gram of liquid, then the work which can be obtained external to the system during the evaporation of one gram will be $p(v_g - v_l)$, where v_l is the specific volume of the liquid, v_g the specific volume of the resulting gas, and p the vapor pressure of the liquid. Applying the second law of thermodynamics, namely, $q = T\frac{dA}{dT}$, it follows that

$$l = T\left(\frac{dp}{dT}\right)(v_g - v_l).$$

This equation is known as the Clapeyron-Clausius equation. As the volume of the liquid can be neglected at low vapor pressures, the equation for a gram molecule of a gas becomes, since under such circumstances $pv_g = RT$,

$$\lambda = \frac{RT^2}{p}\frac{dp}{dT},$$

where λ is the latent heat of evaporation per gram mol. and, on integration,

$$lnp = -\frac{\lambda}{R}\cdot\frac{1}{T} + I.$$

This equation represents with exactness the relation between the pressure and temperature over the temperature range where the latent heat of evaporation may be taken as being constant and the gas laws are obeyed That this range of temperature is very short follows from the previous consideration of the latent heat of evaporation. This quantity is itself dependent on the temperature, diminishing with rise in temperature until, at the critical temperature, it actually becomes zero.

Nernst[1] has suggested an empirical relationship giving the connection between the latent heat of evaporation per mol., λ, and the temperature in which he puts

$$\lambda = (\lambda_0 + 1.75RT - \epsilon T^2)\left(1 - \frac{p}{p_c}\right),$$

giving, when substituted in the Clapeyron-Clausius equation,

$$lnp = -\frac{\lambda_0}{RT} + 1.75lnT - \frac{\epsilon}{R}T + I,$$

where I is the integration constant. This empirical relationship represents the vapor pressure curve over a large range of temperatures. It will be noted that it has the correct form in the critical state for then the expression $\left(1 - \frac{p}{p_c}\right)$

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[1] *Gött. Nachr.*, 1 (1906).

is equal to zero and λ is therefore zero. Three characteristic constants have to be determined for each substance.

Although van der Waals' equation does not give any information in regard to the vapor pressure of a liquid, some speculation may still be made concerning the vapor pressures of liquids relative to one another. In Fig. 2, the experimental curve over that portion where the two phases coexist is approximately the average of the theoretical curve over the same range. This can be expressed by writing

$$\int_{v_l}^{v_g} p\,dv = p(v_g - v_l).$$

Substituting the value for p given by van der Waals' equation, viz.,

$$p = \frac{RT}{(v - b)} - \frac{a}{v^2},$$

and integrating, we obtain

$$RT\ln\frac{(v_g - b)}{(v_l - b)} + \frac{a}{v_g} - \frac{a}{v_l} = p(v_g - v_l).$$

Dividing each side by $p_c v_c$, and replacing a, b, and R by the critical constants, it follows that

$$\frac{8}{3}\frac{T}{T_c}\ln\frac{\dfrac{v_g}{v_c} - \dfrac{1}{3}}{\dfrac{v_l}{v_c} - \dfrac{1}{3}} + 3\frac{v_c}{v_g} - 3\frac{v_c}{v_l} = \frac{p}{p_c}\left(\frac{v_g}{v_c} - \frac{v_l}{v_c}\right),$$

an equation in which the characteristic constants of the substance have disappeared. From what has been said in the preceding section, the critical volumes, measured at corresponding temperatures, are the same for all substances whether they are in the gaseous or liquid state. It follows that, at corresponding temperatures, the corresponding pressures, in this case the vapor pressures, will be the same. This has been tested by Ramsay and Young[1] and found to be true for a large number of substances. If p_1 and p_2 are any two vapor pressures of a liquid at temperatures T_1 and T_2, then $\frac{T_1}{T_c}$ and $\frac{T_2}{T_c}$, the corresponding temperatures, must be the same for any other liquid which has vapor pressures p_1 and p_2 respectively. Hence, $\frac{T_1}{T_c} \div \frac{T_2}{T_c} = \frac{T_1}{T_2}$ should be the same for all liquids. Ramsay and Young measured the temperatures at which the pressures were 76 and 20 cms. respectively, and found the ratio of these temperatures to be a constant, 1.11, for a large number of liquids. However, the universality of this law is not confirmed when very different substances are compared; for example, the temperatures at which the vapor pressures of liquid hydrogen are 76 and 20 cms. are respectively 20.2° and 16.37° K., giving a ratio 1.23. Ethyl alcohol at these pressures has the ratio 1.09. That this deduction from van der Waals' equation is only partially confirmed by experiment is probably intimately connected with the fact that two phases are in existence and that the transition from one phase to another is by no means abrupt. This involves a consideration of the phenomenon of surface tension.

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[1] Young, *Phil. Mag.*, (5) **33**, 153 (1892).

One deduction can be made from the theorem that corresponding pressures of all liquids are the same at corresponding temperatures. Attention has already been drawn to the fact, based on experimental evidence, that the boiling points of liquids, that is, the temperatures at which their vapor pressures are atmospheric, are all approximately at the same corresponding temperature, namely, 0.62 on the corresponding temperature scale. Since

$$\lambda = RT^2\frac{dlnp}{dT},$$

$$\frac{\lambda}{T_B} = R\frac{dlnp}{dlnT_B} = R\frac{dln\frac{p}{p_c}}{dln\frac{T_B}{T_c}}.$$

This number must be a constant for all liquids at corresponding temperatures, that is, $\frac{\lambda}{T_B} = K$. Trouton[1] had already established the truth of this relationship empirically and evaluated the constant as being equal to 20.7. This is known as Trouton's rule.

Vapor Pressure and External Pressure: In the preceding sections, vapor pressure has been considered with a liquid in contact with its saturated vapor alone. A condensed system, solid or liquid, may, however, exist under a pressure different from that of its own vapor. For example, if the vapor contains an indifferent gas, the total gas pressure is the sum of two pressures, that of the vapor and that of the foreign gas. This is, indeed, the normal circumstance in a vessel containing air admixed with vapor in equilibrium with the liquid. Under such circumstances the vapor pressure of the liquid is different from that in the isolated liquid-vapor system. The equation connecting vapor pressure and external pressure was derived by Willard Gibbs in 1876.[2]

Let p be the ordinary equilibrium pressure in a system composed of a liquid (or solid) and its vapor. Let v and V be the respective specific volumes of condensed system and vapor under the pressure p. By exposing the liquid to a pressure $P + p$, let the corresponding values for the several magnitudes become p', v' and V'. Let it be assumed that the compressibility of the liquid can be given by an equation of the form

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[1] Trouton, *Phil. Mag.*, (5) **18**, 54 (1884).

[2] Cf. Partington, Thermodynamics, D. Van Nostrand (1924).

$$v' = v - v\kappa P,$$

where κ is the coefficient of compressibility. The desired relationship may now be established by means of an isothermal reversible cycle.

(1) Unit mass of the liquid at pressure $P + p$ is evaporated to produce vapor at pressure, p'; the work done,

$$A_1 = p'V' - (p + P)v(1 - \kappa P).$$

(2) The vapor at p', V' is expanded to p, V, the work done,

$$A_2 = \int_{V'}^{V} p\,dv = pV\,ln\,\frac{p'}{p}\cdot$$

(3) The vapor at p, V is now condensed, the work done,

$$A_3 = -p(V - v).$$

(4) The liquid is now compressed to $P + p$; the work done,

$$A_4 = -\left(p + \frac{P}{2}\right)P\kappa v.$$

The cycle is now complete and so

$$A_1 + A_2 + A_3 + A_4 = 0.$$

If we assume Boyle's Law $pV = p'V'$, and neglect all terms containing κp, we obtain

$$pV\,ln\,\frac{p'}{p} = Pv\left(1 - \frac{P\kappa}{2}\right)$$

or

$$\frac{p'}{p} = e^{\frac{Pv}{pV}(1 - P\kappa/2)}$$

$$= 1 + \frac{Pv}{pV} + \text{etc.}$$

If P is not very great, the higher terms may be neglected and

$$p' - p = \frac{Pv}{V}\cdot$$

If the increase in pressure applied to the liquid is δP and the consequent increase in vapor pressure is δp, the equation becomes

$$\left(\frac{\delta p}{\delta P}\right)_T = \frac{v}{V}\cdot$$

The vapor pressure of any liquid (or solid) is increased by compression of the condensed phase. An alternative proof of this relationship has been given by Porter in a general treatment of osmotic pressure and lowering of vapor pressure.[1]

Since $\frac{v}{V}$ is a very small fraction for all small values of δP, it follows that the variation in the vapor pressure with external pressure is generally negligibly small. Thus, the vapor pressure of a liquid under its own saturated vapor will not be sensibly different from that when the liquid is exposed to the pressure of the atmosphere. At the super-pressures which are now becoming familiar in actual practice, variations in the vapor pressure will be manifest. This may be illustrated by reference to the case of water and water vapor. Callendar's equation of state for water vapor is

$$V = 4.548\frac{T}{p} - 26.3\left(\frac{373}{T}\right)^{\frac{10}{3}} + 1.0;$$

for liquid water,

$$v = 1.002(1 - 4.0 \times 10^{-5}P),$$

the pressures in each case being stated in atmospheres. Inserting these equations in the expression

$$\frac{\delta p}{\delta P} = \frac{v}{V},$$

there follows, for a temperature of 20° C.,

$$\int_{p_0}^{p}\left(\frac{1333}{p} - 57.8\right)dp = 1.002\int_{p_0}^{P}(1 - 4.0 \times 10^{-5}P)dP,$$

whence, for $p_0 = {}^{17}/_{760}$ atm. at 20° C.,

$$3062 \log\frac{p}{p_0} - 1.329\frac{p}{p_0} + 1.33 = P - 2.0 \times 10^{-5}P^2.$$

From this expression it may be calculated that the ratio $\frac{p}{p_0}$ is 1.2 at a pressure $P = 300$ atmospheres approximately. In other words, under the pressure of an inert gas equal to 300 atmospheres the vapor pressure of water at 20° C. increases by about 20 per cent.

Surface Tension: It has already been shown that, in a gas, the surface molecules are not truly representative of the average condition of the molecules as a whole. The constant a of van der Waals' equation is representative of a surface tension correction which has to be made. In a discussion of critical phenomena, the nature of the surface tension existing at the surface liquid-vapor has already been discussed and this will now be somewhat further amplified. The molecules at the surface are under a differential force in a direction towards the main body of the liquid. Fast moving molecules are continuously moving through the surface into the vapor. Besides those whose kinetic energy is sufficient to carry them beyond the range of the attractive force of the liquid there are some whose velocity carries them just short of this distance. The change in density from liquid to gas cannot therefore be abrupt; there will be planes parallel to the surface in which the average density is intermediate between that of the liquid and the gas The existence of this layer of intermediate density is evidenced physically by the creation of a fresh surface of liquid when it is found that the surface formation requires the addition of heat energy in order to be isothermal. Extending the surface necessitates that a certain number of molecules of the liquid form this layer of intermediate density and therefore expand against the force of molecular attraction. A cooling will result paralleling the cooling of a gas obtaining when a gas expands, the Joule-Thomson effect To form a fresh surface isothermally, work has to be done against the surface tension and heat has to be added to prevent cooling By substitution in the Gibbs-Helmholz equation, it follows that

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[1] *Proc. Roy. Soc.*, **79A**, 519 (1907); **80A**, 457 (1908).

$$q = \gamma - \Delta U - T\frac{d\gamma}{dT},$$

where q is the heat added, γ is the surface energy and ΔU the change in total energy of the surface

In order to proceed with a consideration of surface tension phenomena the practical definition of surface tension involved in its methods of measurements is of importance Surface tension is defined as the force in dynes per unit length of surface of liquid in a direction parallel to the surface If one imagines a film of liquid bounded on three sides by a rod bent into the form of a U, and on a fourth side by a movable rod, then, assuming the absence of friction, the surface tension will tend to contract the film, and a force, F, has to be applied to keep it in place By the above definition,

$$F = 2\gamma l,$$

where γ is the surface tension and l the length of the movable rod in contact with the film The factor 2 takes into account the two sides of the film Suppose the rod be moved through a distance x, so that the film is extended and its surface increased by $2xl$, then the work done is

$$Fx = 2x\gamma l,$$

so that the energy required to create unit area of surface will be γ ergs, and the potential energy per unit area due to the surface tension is γ

It is not quite obvious that the definition of surface tension given above, i.e , the measurement of a force parallel to the surface, is a relative measurement of this downward field of force which has hitherto been spoken of as giving rise to surface tension. A diagram of what takes place upon the creation of a new surface will aid in showing the connection between the two. In Fig. 3, one wall of the containing vessel is moved in such a way as to extend the surface. Molecules from a region of the liquid in which they were not subject to a differential or resultant force have to be pulled up to the surface against the resultant force in order to create the new surface. In the diagram, this is represented by an imaginary pulley at the surface with an imaginary string attached to a molecule which is being drawn up against the downward force, the work done being equal to the potential energy which the molecule finally has in virtue of its new position.

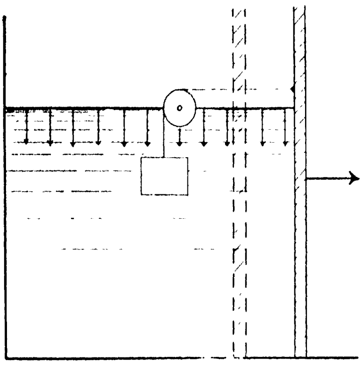

FIG. 3

The method of employing the force exerted by a film for measuring surface tension is not generally practicable for obtaining accurate results, but, in the case of a liquid having a small surface tension, it can be used. Very interesting information has been obtained thereby in regard to the range through which molecular forces are effective. As the film formed by a definite quantity of liquid is extended more and more, its thickness decreases. When the thickness of the film becomes less than twice the diameter of the range of molecular forces, the surface tension should obviously decrease as well. It was found by Rucker [1] that the thickness of the film had no influence on the surface tension until the thickness had been diminished to 10^{-6} cm. The surface tension was found to diminish with further decrease in thickness of the film. The surface tension of salt water measured at the surface of the ocean gives exactly the same value as the surface tension measured by means of a thin film of this water. It may be seen, therefore, that the molecular forces have a very small range, and that the effect of a resultant force is confined to relatively few layers of molecules in the surface.

Two methods are available for the accurate determination of surface tension in absolute values: the rise in the capillary tube and the drop weight method. It is instructive to consider the surface tension relationships involved in these two methods. To obtain these, the potential energy of the surface will be taken into account in connection with the principle that any system will tend to arrange itself in such a way that the potential energy will be a minimum. This principle is illustrated by the tendency of a drop of liquid to assume a spherical shape, because the sphere has the smallest area of any form which a given mass may take and has, therefore, the smallest potential energy so far as surface tension is concerned. In the case of a small drop of mercury resting on a plane surface the drop is not truly spherical because the spherical form would raise its center of gravity and thus increase the potential energy due to gravity. The drop of mercury will therefore take a form such that the sum of the potential energies due to surface tension and to gravity is a minimum.

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[1] Rücker and Reinold, *Phil. Trans.*, 177, 627 (1886).

The surface tension of a liquid will depend on the medium with which it is in contact; the surface tension at a surface liquid-glass is different from that at the surface liquid-air. Suppose a liquid in contact with a glass plate reaches the equilibrium position and the angle of contact is θ. If γ_l is the surface tension of a liquid-air, γ_g the surface tension of the glass-air, and γ_{lg} the surface tension at the surface liquid-glass, then, if the liquid be given a small displacement so that an additional area dx of glass is covered, the increase in potential energy is

$$dx\gamma_{lg} + dx\gamma_l \cos\theta - dx\gamma_g.$$

But, if the system was in equilibrium and consequently the potential energy a minimum, a small displacement will not change the potential energy and the increase in potential energy will be zero. In other words,

$$\gamma_l \cos\theta = \gamma_g - \gamma_{lg}$$

Now, if a capillary tube, of radius r, has one end immersed in a liquid, and the latter reaches equilibrium after rising to a height h, the angle of contact between liquid and glass being θ, a small displacement will not change the potential energy of the system. Thus, if the liquid be supposed to rise a small distance dx, the change in potential energy due to the forces of gravity and surface tension can be equated to zero. Therefore,

$$2\pi r(\gamma_{lg} - \gamma_g)dx + g\pi r^2 dx\rho h + gv\rho dx = 0,$$

where ρ is the density of the liquid, v is the volume of the meniscus, which is approximately equal to $\frac{1}{3}\pi r^3$ if the angle of contact is small. But

$$(\gamma_{lg} - \gamma_g) = -\gamma_l \cos\theta,$$

so that

$$\gamma_l = \frac{r\rho g}{2\cos\theta}(h + \tfrac{1}{3}r).$$

Most liquids make a very small angle of contact with glass so that $\cos\theta$ approaches unity. A liquid like mercury which makes an angle of contact greater than 90° is depressed in a capillary tube in agreement with the negative value of the cosine when $\theta > 90$ degrees. The method of deducing the above relationship brings out the fact that the rise in the capillary tube depends solely on the surface of the liquid and the medium above it in the special case $\theta = 0$, and is then independent of the surface tension between the liquid and the glass. By measuring the height to which the liquid will rise in a tube of known radius the surface tension can be accurately determined. The precautions which have to be taken for an accurate determination have been investigated by Richards.[1]

The drop weight method by itself does not give the absolute values of surface tension. When a drop forms at the end of a tube of radius r (this radius refers to the circle of contact between the drop and the tube), at the moment before its size is such that the drop will fall, this drop is in a state of equilibrium. A small displacement will not alter its potential energy. Suppose the drop is displaced through a distance dx, the change in potential energy will then be

$$- mgdx + 2\pi r dx \gamma_l - \pi r^2 \frac{\gamma_l}{r},$$

where m is the mass of the drop. The first term represents the decrease in potential energy due to gravity, the second that due to surface tension, and the third the work done against the pressure exerted by surface tension, for the latter is given by $\frac{\gamma_l}{r}$. Equating this to zero, it follows that

$$\gamma_l = \frac{mg}{\pi r},$$

so that, by measuring the weight of a drop and knowing the radius, the surface tension can be calculated. This relationship is based on the assumption that the displacement of the drop at the moment of fall is such that the liquid between the drop proper and the tube has the form of a cylinder, whereas actually it will have a conical shape, the curvature depending both on the radius of the tube and the surface tension of the liquid. The surface tension, γ_l, is therefore equal to a constant times the weight of the drop where this constant has to be evaluated. This has been done by Harkins.[2] The constant is only slightly affected by the surface tension and a correction can therefore be applied when the surface tension is approximately known. Many of the determinations of surface tension prior to the investigations of Richards and Harkins are incorrect by as much as twenty per cent due to the neglect of taking into account the precautions advocated by these investigators.

From what has been said in regard to latent heat of evaporation and surface tension, it would seem probable that the two are related. The latent heat of evaporation is a measure of the work done in bringing the molecules from the interior of the liquid into the vapor above. This work consists in bringing molecules first to the surface against the field of molecular force, and in then moving them out of this field of force, together, finally, with the work done against the external pressure. The latter has a definite value, namely, pV, where p is the vapor pressure and V the volume formed. When this is subtracted from the total latent heat, the remainder has been called the internal latent heat. The latter should be proportional to the surface energy, and this has been found to be the case.[1] Again, since the surface tension is an indication of the magnitude of molecular forces of attraction, it should be related to the critical temperature, for it has been shown that the critical temperature is a measure of the molecular force from the point of view that the higher the critical temperature, the greater is the kinetic energy which the molecules must have in order to prevent liquefaction by molecular forces. This too has been confirmed, qualitatively at least, by experiment.[2] However, no exact proportionality factor has been found experimentally to exist either for this or for the preceding relationship when liquids are compared whose molecules differ widely with regard to their component atoms and constitution. The nonexistence of exact relationships is of great importance because this, as well as many other apparent difficulties in interpreting the kinetic theory, may possibly be traced to a factor which has not as yet been considered, namely, the orientation of molecules at low temperatures

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[1] *J. Am. Chem. Soc.*, **37**, 1656 (1915). See also *ibid.*, **46**, 1196 (1924).

[2] Harkins, *J. Am. Chem. Soc.*, **38**, 228 (1916).

The variation of surface tension with the temperature has been the subject of much research. With rise in temperature the surface tension decreases, reaching a zero value at the critical temperature For the greater part of the temperature range the relation between surface tension and temperature is nearly linear. As the critical temperature is approached within about 8°, the surface tension varies less rapidly with the rise in temperature. It was shown by Eotvos,[3] and Ramsay and Shields,[4] that the variation of the molecular surface energy with the temperature is a constant This can be represented by the equation

$$\gamma\left(\frac{M}{d}\right)^{2/3} = k(T - 6^\circ - T_c),$$

where M is the molecular weight and d the density of the liquid. The expression $\left(\frac{M}{d}\right)^{2/3}$ for the molecular surface is based on surfaces which contain equal numbers of molecules. The volume $\frac{M}{d}$ contains equal numbers of molecules; M, the molecular weight, refers not to the theoretical molecular weight, but to the conglomerations of atoms in the liquid whose center of gravity has freedom of translatory movement in the liquid along any three axes at right angles. Ramsay and Shields have shown that, for normal liquids, k has a constant value 2.12, independent of the nature of the liquid. A number of liquids have since been found which give exceptional values for k. If these exceptions are neglected for the moment, then this relationship, if really true, divides liquids into two classes: those whose molecules in the liquid state are associations of vapor molecules, and those which are not. Water belongs to the first class,

[1] Edser, Fourth Report of Brit Assoc on Colloid Chem , page 99, 1922

[2] Edser, Fourth Report of Brit Assoc. on Colloid Chem , page 99, 1922

[3] Eotvos, *Wied. Ann* , **27**, 448 (1886).

[4] Ramsay and Shields, *Phil. Trans* , **A 184**, 647 (1893).

for in order to obtain

$$\frac{d\left[\left(\frac{M}{d}\right)^{2/3}\gamma\right]}{dT} = 2.1,$$

M must equal 36 or 54, whereas, in the vapor, M has the value of 18. This therefore brings up an additional complicating factor in connection with the liquid molecules, namely, the association of molecules to form larger chemical complexes. A similar behavior has already been referred to in the case of gases such as sulphur vapor which apparently did not obey the gas law. There the discrepancy was explained on the basis of molecular complexity. In a similar way the liquids with associated molecules cannot be expected to give results consistent with the kinetic theory. This is illustrated by the application of Trouton's rule to liquids whose variation of molecular surface energy with the temperature shows that they are associated. Invariably the constant for Trouton's rule is larger than 20.7 for these liquids.

Perhaps the difficulties brought up by association of molecules will be made apparent by the table of physical properties of a number of compounds having nearly the same theoretical molecular weight.

TABLE II

	Total Surface Energy	Critical Temperature	Ramsay and Shields Constant	Trouton's Constant
Ethylene Oxide....	73.1	465.0	1.84	21.1
Ethyl Alcohol......	16.0	513.6	1.2	26.0
Acetaldehyde.. ...	56.6	454.5	1.4	21.5
Methyl Ether	55.1	402.6	2.0	21.2

The first column gives the total surface energies. Ethyl alcohol has by far the smallest total surface energy; ethylene oxide the greatest. The second column gives the critical temperatures which were quoted as being a measure of the molecular forces of attraction. These values are not at all in agreement with the surface energy because ethyl alcohol has the highest critical temperature, much greater than that of ethylene oxide. Methyl ether, which has the lowest critical temperature, has a greater molecular surface energy than alcohol. The explanation is given by the value for the Ramsay and Shields constant (calculated on the basis of theoretical molecular weight) and Trouton's constant, given in the third and fourth columns. From these values it is apparent that ethyl alcohol at low temperatures in the liquid state is associated. The surface energy and the critical temperature of ethyl alcohol are constants of two distinctly different substances. The critical temperature is a measure of the molecular force of attraction between C_2H_5OH molecules; the total surface energy is a measure of the molecular force of attraction between $(C_2H_5OH)_2$ molecules. In the case of methyl ether there is no change in molecular complexity, and the critical temperature and total surface energy are both truly representative of the molecular forces of attraction of one and the same liquid. Hence, a comparison of the physical constants of liquids, with a view to obtaining an insight into the magnitude of molecular forces of attraction, is only valid in the case of liquids with unassociated molecules.

It is of interest to see plainly the influence of surface tension on the vapor pressure by considering a curved surface. Suppose a molecule close to the surface of the liquid has a velocity sufficiently great to carry it out of the surface. Three cases may be considered, a concave, a flat, and a convex surface, represented by Cases 1, 2, and 3, in Fig. 4. Consider molecules which are equidistant from the surface in each case. These molecules may be moving in any direction but the chance of their taking a direction which will bring them to the surface for a definite velocity will be given by the three angles θ_1, θ_2, and θ_3. Obviously the best chance for emerging from the surface is in Case 3, the convex surface; obviously, also, the molecules leaving the convex surface will be soonest out of the molecular range of attraction which is proportional to the areas of the shaded regions in the diagram. Hence, since the vapor pressure is dependent on the number of molecules getting out of the liquid, the vapor pressure will be dependent on the curvature of the surface as well as on the surface tension. It follows that the vapor pressure of small drops of liquid is greater the smaller the radius of the drop.

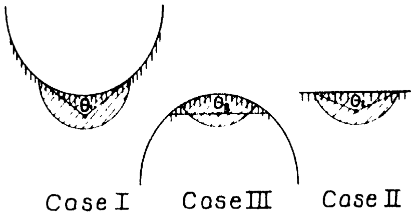

Fig. 4

It is not difficult to establish the exact relationship between the vapor pressure and curvature. Suppose a liquid rises to a height h, in a capillary tube whose radius is r, then, the vapor pressure of the concave surface must be less than that of the flat surface because, at the height, h, the pressure of the vapor is less by the weight of a column of vapor of that height than the vapor pressure of the liquid at the flat surface. In fact, if p' is the vapor pressure of the concave surface, p that of the flat surface, and ρ the density of the vapor, then $p - p'$ must equal ρh, otherwise equilibrium would never result and a perpetual motion machine be possible. The variation of gas pressure with distance in a direction perpendicular to the force of gravity has been shown, in Chapter III, to be given by

$$ln \frac{p}{p'} = \frac{M}{1033 \times 82T} h.$$

But

$$\gamma = \frac{r\rho gh}{2 \cos \theta},$$

so that

$$ln \frac{p}{p'} = \frac{2 \cos \theta \gamma M}{1033 \times 82 T r \rho g}.$$

If the material of the tube is such that the liquid makes an angle of contact of 180°, the liquid will be depressed in the tube, for then cos θ is equal to $- 1$, and

$$ln \frac{p'}{p} = \frac{2 \gamma M}{1033 \times 82 T r \rho g}.$$

This gives the vapor pressure of a small drop, and since, when r is exceedingly small, it follows that p' is very large, the ease with which vapors can be cooled below their condensing temperature is easily explained by the high vapor pressure requisite for the initial drop formation. On the other hand, the vapor pressure of a concave surface of the liquid will be very small when this concave surface is formed, say, by a small bubble of the vapor itself, and, in addition, since the pressure p in a small bubble must be greater than the hydrostatic pressure by an amount given by the equation

$$p \pi r^2 = 2 \gamma \pi r,$$

it is easily understood why liquids can be superheated below their surface. As a matter of fact, it would appear that the formation of a vapor bubble below the surface could not start, since the vapor pressure required is inversely proportional to the radius, and the pressure required in addition to the ordinary vapor pressure is also inversely proportional to the radius. However, both depend on the surface tension and this will decrease when the diameter of the bubble equals the effective range of molecular attraction.

The Orientation of Molecules: The idea of the polar molecule is almost as old as the molecular theory itself. The basis of this idea is that the field of molecular forces of attraction does not proceed uniformly from the center of the molecule but may be concentrated in the neighborhood of one of the atoms composing the molecule. The oxygen atom has long been recognized as one whose field of force is not completely neutralized by the fields of force of neighboring atoms held in direct chemical combination with it. Formic acid, for instance, may be looked upon as having a large field of molecular attraction resulting in a high surface tension, high critical temperature, etc. Ethane molecules have a very small attraction for one another, as is evidenced by their physical constants. A molecule composed, so to speak, of both, namely, propionic acid, will then be a polar molecule, one in which the molecular force of attraction is more concentrated in one particular part, so that if these molecules are oblong in shape, the field of force around one end, the $-$ COOH end, will be more pronounced. From the modern point of view of an atom, composed of electrons distributed around a positive nucleus at the center, the Lewis, Langmuir or Thomson[1] structure of the molecule may be represented as a system of electrons and positive nuclei the relative positions of centers of gravity of each of which can be estimated from the space arrangement of the atoms in the molecule. From this point of view, a molecule is polar when these two centers of gravity are some distance apart, and such a molecule can be represented as an electric doublet with the total negative charge at one center of gravity and the total positive charge collected at the other. In a very long and complex molecule such as sarcosine, $CH_3NH\ CH_2COOH$, it is necessary to represent the distribution of electricity by a greater number of positions than two. Again, if instead of accounting for the molecular forces of attraction by the static electric charges alone, magnetic fields rising from electronic motion are considered to play a part in molecular attraction, polar molecules can in that case be represented by magnetic doublets.

This is not the place to discuss the relative merits of the mechanism giving rise to molecular attraction, a subject which properly belongs to a discussion of the theories of atomic structure It is sufficient to say that on the basis of any of the hypotheses quoted, polar molecules are conceivable on the definition of unequal distribution of molecular attraction The existence of molecular orientation logically follows the conception of the polar molecule. Suppose that a number of molecules are placed in a row anchored at points equidistant from one another but free to rotate, they would be orientated in the same direction. On the electric doublet basis, for instance, the positive of any one molecule would be adjacent to the negative of its neighbor In three-dimensional space, orientation would take place, but in a different manner. The principle governing an orientation is that the distribution of positive and negative electricity is such that it will be most uniform and the potential energy therefore a minimum Thus, a three-dimensional system with equidistant molecules will, in a special case depending on the distance between the positive and negative centers of gravity in the molecule and the distance between the molecules, arrange itself so that each positive will tend to surround itself by eight negatives and vice versa In such a system, where the molecules do not rotate, the forces of mutual attraction holding the system together as a whole may be very considerable, independently of any vibratory movement which the molecules may have But once the molecules are given rotational movement and translatory movement (the latter implying that their average positions do not remain fixed relative to one another), then the force of mutual attraction will diminish, and the more so the greater their rotational and translatory movement. In a gas at high temperature the molecular orientation is relatively small. As the temperature is lowered, and particularly in a liquid where the molecules are close together, partial regional orientation may take place. By partial orientation it is implied that, although the axis of a molecule will pass through all directions relative to a line fixed in space, it will on the average take up a direction influenced by, and influencing the direction of the axes of its neighboring molecules. If this is so, it follows from what has been said above that the sum total of the molecular forces of mutual attraction of the molecules will vary with the temperature, increasing with lower temperature.

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[1] J. J Thomson, *J Franklin Inst*, **195**, 593 (1923) Lewis, *J. Am. Chem. Soc.*, **38**, 762 (1916). Langmuir, *J. Am. Chem. Soc.*, **41**, 868 (1919).

Phenomena have been observed which are in line with the observed considerations. Certain substances such as cholesterol acetate and *p*-azoxyanisole, whose molecules are particularly polar, melt to form milky liquids the milkiness of which disappears with rise in temperature. Such liquids are anisotropic, and the misleading name of "liquid crystals" has been given to them by O. Lehmann.[1] The turbidity and optical properties were explained by Lehmann on the basis that these substances melted first of all to form large aggregates each of which was a crystal, the disappearance of turbidity being accounted for by the melting of these small crystals in turn at higher temperatures. This explanation is in opposition to the kinetic theory conception of a liquid. The liquid crystals would have to be enormous aggregates in order to give the optical phenomena observed. Yet, these liquid crystals have low viscosity (whereas liquids with large molecules have very large viscosities), and their variation of molecular surface energy with the temperature is in agreement with this low molecular weight. In fact, the variation of their physical properties, except for the rather sharp disappearance of turbidity, is continuous. In order to correlate his theory of liquid crystals with the properties of ordinary liquids, Lehmann was willing to abandon the whole kinetic theory of liquids. The real explanation of liquid crystals is given by the regional orientation of the molecules of the liquid taking place in a manner discussed above, an hypothesis which was put forward for the first time by E. Bose.[2]

The distinction between regional orientation and a small crystal is that all the atoms in a small crystal may be looked upon as belonging to the same molecule, whereas in a region where orientation has taken place the molecules retain their identity and have translatory and rotational energy possessing only an averaged orientation for a very short time. The regions in a liquid are not sharply defined, but pass gradually and without any discontinuity into one another. These regions may be momentarily represented by arrows giving the direction of orientation. Contour lines around these arrows would represent the gradual diminution of orientation and blending with the direction of a neighboring region. These contour lines would be continuously shifting, orientation arrows disappearing and new ones appearing in fresh places. In the case of *p*-azoxyanisole the temperature at which visible turbidity still exists increases with the pressure.[3] This is in agreement with the above theory, since increased pressure brings the molecules closer together and increases the chance and probability upon which regional orientation depends. These "liquid crystals," i.e., liquids with visible turbidity, are liquids with exceedingly polar molecules. It is probable that regional orientation, though far less pronounced, will exist for other liquids whose molecules are not quite so polar. The saturated fatty acids exhibit a slight turbidity just above their melting points which gradually disappears with rise in temperature. The longer the fatty acid the more pronounced is the turbidity, being very marked in the case of palmitic acid, for instance, and not visible in the case of acetic. Nevertheless, it is probable that a certain amount of regional orientation exists in the latter. Recently an important contribution to this subject has been made by the study of X-ray diffraction caused by liquids,[1] and important results may be expected in the near future from this line of research. The variation of the extent of the molecular orientation with the temperature has an important bearing on the variation of molecular forces of mutual attraction and is a factor which may account for some of the discrepancies of van der Waals' theory applied to liquids.

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[1] *Z. physik. Chem.*, **71**, 35 (1910).

[2] *Physik. Z.*, **9**, 708 (1908); **10**, 32, 230 (1909).

[3] Hulett, *Z. physik. Chem.*, **28**, 629 (1899).

The regional orientation does not give a resultant orientation for the liquid as a whole. Only when a small enough volume is chosen will the average directions of the molecular axes give a momentary predominant direction; in a neighboring region the predominating direction may be just the opposite. This is what gives rise to turbidity in the so-called "liquid crystal" liquids. Another type of orientation confined to the molecules in the surface layer has recently received considerable attention. The fascinating experiments of Rayleigh, Devaux, Debrouste and, more recently, Langmuir[2] on the areas of water over which small portions of fatty acid can spread show that the area of contact of a fatty acid molecule is independent of the length of the carbon chain, proving that these molecules are orientated. Langmuir extended this idea to all liquids whose molecules were at all polar. The orientation will take place in such a way that the potential energy will be a minimum, that is, the gradient of the differential force between liquid and vapor will be least abrupt. Thus, if the main force of mutual attraction is confined to one end of a molecule, that end will tend to orientate the molecule in such a way that it is closest to the main body of the molecules in the liquid. This latter hypothesis was developed independently by Harkins[3] who collected experimental data in its support. If the molecules of a fatty acid are again taken to illustrate this point, they would all tend to have the hydrocarbon part of the molecule forming the surface of the liquid and the carboxyl groups pulled towards the main body of the molecules of the liquid. If it is remembered that the arrangement at the surface is dependent on a dynamic equilibrium, it is easily seen that the movement of the molecules will tend to counteract the orientation, just as agitation counteracts regional orientation. The surface orientation, therefore, treated statistically, means that, on the average, over a long period, the axis of the molecules will occupy one position in preference to another. Experimental evidence in support of the idea of surface orientation is given by the examination of the surface energies of homologous series such as the fatty acids. The question of the temperatures at which the surface tensions should be compared is answered by comparing the total surface energies, which have already been defined as $\gamma - q_0$, where q_0 is the heat required for isothermal expansion of unit area. Now, $q_0 = T\dfrac{d\gamma}{dT}$, and the variation of the surface tension with the temperature is practically linear and can be expressed by $\gamma = \gamma_0(1 - aT)$. Hence $\gamma - q_0 = \gamma_0$ is independent of the temperature.

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[1] Keesom and de Smedt, *Proc. Acad. Sci. Amsterdam*, **26**, 112 (1923).

[2] Langmuir, *Met. Chem. Eng.*, **15**, 468 (1916); *J. Am. Chem. Soc.*, **39**, 1848 (1917).

[3] *J. Am. Chem. Soc.*, **39**, 354, 541 (1917).

TABLE III

	$\left(\gamma - T\dfrac{d\gamma}{dT}\right)$	Ramsay and Shields Constant
Formic	63.6	0.90
Acetic	58.2	1.30
Propionic	56 9	1.44
Butyric	54.4	1.57
Lauric	54.6	2.57
Palmitic	54.5	2.93
Stearic	54.8	3.04

In Table III the values of the surface energies of some of the fatty acids are given. It will be noticed that the surface energy decreases with increase in length of carbon chain and tends to reach a minimum value. This is in agreement with the orientation at the surface. Formic acid has the largest surface energy and little orientation will probably exist. With increasing length of carbon chain the tendency towards orientation increases with a consequent diminution of potential energy, a limiting value being reached with butyric acid.

The third column in Table III contains the Ramsay and Shields constants for the variation of molecular surface energy calculated on the basis of the theoretical molecular weights. If the variation of surface energy with the temperature is a constant for a molecule independent of its nature, then formic acid is associated to an extent given by $\left(\dfrac{2.1}{.9}\right)^{3/2} = 3$. When the higher acids are considered, a similar calculation leads to the apparently absurd result that these acids are dissociated. In the case of stearic acid, for instance, $\left(\dfrac{2.1}{3}\right)^{3/2} = \frac{1}{2}$. From the point of view, however, of the orientation at the surface, dissociation need not be assumed to explain the experimental facts. The calculation of the molecular surface to obtain the Ramsay and Shields constant is given by $\left(\dfrac{M}{d}\right)^{2/3}$, that is, it is assumed that the molecules are spherical or cubical in shape. Orientation will mean a far larger number of molecules per unit area in the case of the long molecules. The longer the carbon chain the greater the Ramsay and Shields constant, which is in agreement with the experimental data quoted above. The stearic acid molecules may even be associated as the formic acid molecules are, and orientation will still account for the high value of the constant.

In the beginning of this section mention was made that the polarity of a molecule might possibly be represented by either a magnetic or electric doublet. An examination of the dielectric constants seems to point to the existence of electric doublets, since the more polar compounds have the greater dielectric constant. When a liquid whose molecules are polar is placed in an electric field, this electric field will tend to orientate the molecules if these are electric doublets. The orientation will be in a direction such as to create alternate layers of positive and negative electricity throughout the liquid, the positive and negative layers obviously taking relative positions so as to diminish the intensity of the electric field. Thus, the mechanism giving rise to the dielectric constant can be easily explained. On the other hand, *p*-azoxyanisole, which is a turbid liquid in the neighborhood of its melting point, has this turbidity diminished when placed in a powerful magnetic field,[1] showing that the regional orientations have been given a common direction. Artificial orientation has been caused in this case by a magnetic field, so that the molecules might be taken as magnetic doublets. It may be found eventually that both magnetic and electric doublets exist in polar molecules. However that may be, the long prevailing idea of a non-uniform molecular field of force surrounding a molecule is one of the factors which must be considered whenever molecular forces are brought into play in connection with the liquid state of aggregation.

Molecular Orientation in Films: Reference was made in the preceding section to the experiments of Langmuir, by means of which the orientation of molecules at liquid surfaces was established. One phase of this work, the orientation of molecules in films of molecular thickness, has been subjected to an extended investigation by N. K. Adam [2] and the results warrant a separate section because of the highly instructive information which they have given with regard to molecular dimensions and molecular forces.

The experimental method used was the same as that designed by Langmuir. It is shown diagrammatically in plan and elevation in Fig. 5. A trough, *A*, is filled with water, separated into portions by two strips, *B* and *C*, of paraffined copper immersed in the water to half their thickness. Strip *B* is supported by the walls of the trough and makes contact with the sides. Strip *C* is fastened rigidly to a beam balanced on a knife edge, *F*, which is supported by a stand not shown in the diagram. On one end of the beam a pan is fastened on which weights can be placed, and a counterpoise weight is attached to the other end. Strip *C* does not touch the sides of the trough and is free to move in either direction, *S* or *S'*. When pure water is in contact with both sides of strip *C*, the balance is in its zero position, adjustment of the weights having been made so as to bring strip *C* directly under the knife edge. On placing an oil, which spreads over water, between strips *B* and *C*, the surface tension forces on *C* are upset; that of the pure water predominates and the strip tends to move in direction *S*, but is prevented from doing so by the addition of the proper weights to the balance pan. To stop the oil from getting past the ends of the strip *C*, two jets of air are played at points *D* and *D′*. These jets are maintained at constant speed, and any effect they have on strip *C* is adjusted in the first instance, before adding the oil to the water surface.

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[1] Mauguin, *Compt. Rend.*, **152**, 1680 (1911).

[2] *Proc. Roy. Soc.*, **99 A**, 336 (1921); **101 A**, 452, 516 (1922); **103 A**, 676, 687 (1923).

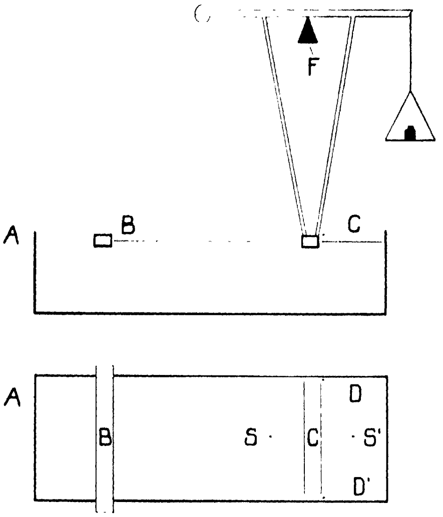

FIG. 5. Apparatus for Measurement of Film Characteristics

A description of the precautions that have to be taken, such as the assurance of an uncontaminated water surface, will not be detailed. The procedure to form the film consists in placing a known weight of the substance out of which the film is to be formed, dissolved in a few drops of benzene, on the surface between the strips *B* and *C*, the former being at the far end of the trough. After the benzene has evaporated, the strip *B* is gradually moved toward *C*. Provided a small enough quantity of substance has been used, no effect is noted on strip *C* until the area between *B* and *C* has been diminished beyond a certain point. After that, weights are placed in the pan to keep *C* in its zero position, the areas between *B* and *C* and corresponding weights being tabulated. The weights are expressed in dynes per unit length of *C*, measured in the direction *S′*, and the area, measured in square centimeters, is divided by $\frac{m}{M}\cdot 6.06 \times 10^{23}$, where *m* is the weight of the substance composing the film, and *M* its molecular weight. This gives the average area occupied by each molecule.

The first series of substances examined by Adam were the saturated fatty acids, with carbon chains ranging from twelve to twenty-six carbons. Curve I, Fig. 6, was obtained when distilled water was used, and the temperature maintained at 20° C. The attraction of the COOH group for water and the consequent reduction in surface energy caused by the spreading of the acid ensured a dispersion over the surface, one molecule thick. The striking feature found was that curve I was identical, within a few per cent, for all the acids examined. That is, when the area of the film had been reduced to the extent where the molecules were closely packed together, the area occupied per molecule was found to be 21×10^{-16} square centimeters, independent of the length of the carbon chain. When the area was diminished below 21×10^{-16} sq. cms., a slight compression occurred, indicated by the curve *ab*, and then, suddenly, the film was found to collapse, due to the piling up of the molecules of the film. The fact that the molecules occupy the same area independent of the length of the carbon chain, and the fact that the area found (21×10^{-16} sq. cms.) is the area of the cross-section of a CH_2 group estimated in other ways, is conclusive proof of the orientation of the molecules composing the film.

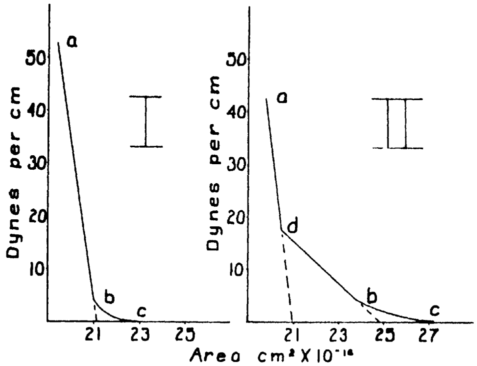

FIG. 6

Naming the polar group the head of the molecule (in the case of the fatty acids, the COOH group), it appears that the head occupies a greater area than the cross-section of the chain. Where the film is spread over distilled water, the cross-section of the chain gives the effective area, because of the different depths to which alternate molecules enter into the water. That this is so was shown by increasing the hydrogen-ion concentration of the water, which diminishes the attraction of the COOH group for the water and forces all these groups to the same level. Curve II shows the result obtained for any saturated fatty acid, spread over $N/100$ HCl solution. The area corresponds to 25 $\times 10^{-16}$ sq. cms., the cross-section of the polar group. Diminution in area increased the lateral pressure on the film molecules and forced the heads to different levels until the carbon chains were again in close contact, corresponding to a cross-section of 21 $\times 10^{-16}$ sq. cms. This is brought out by the point of inflection, *d*, in Fig. 6, curve II.

Table IV shows a number of results selected from a large number of substances examined. Column I gives the name of the substance composing the film; column II the number of carbon atoms; column III the area of the cross-section of the carbon chain; column IV that of the polar group.

TABLE IV

PROPERTIES OF ORIENTED FILMS

	Number of C Atoms	Cross-section		Temperature of Expansion
		Chain	Head	
Myristic acid.... ...	14	21.0	25.1	9°
Stearic acid...	18	21.0	25.1	46°
Behenic acid	22	21.0	25.1	72.5°
Cetyl alcohol	16	21.0	21.7	49°
Stearic nitrile........ ..	18	21.0	27.5	26°
Hexadecyl phenol		21.0	23.7	53°
Octadecyl phenol........		21.0	23.8	66°

It is interesting to note that the area occupied by the head in the case of benzene compounds such as octadecyl phenol, which have a long carbon chain and a polar group in the para position, averages 23.8 $\times 10^{-16}$ sq. cms., which is in agreement with an area of 23.3 $\times 10^{-16}$ sq. cms. as deduced from the measurements of Bragg on the crystal structure of benzene.

At low temperatures the molecules in the film are in direct contact over the whole surface and in this condensed condition are in either the liquid or the solid state. The films show no hysteresis effects and the portion, *ab*, of the curve shown in Fig. 6 does not vary appreciably with the temperature. The lower parts of the curves, *bc*, have the general shape of hyperbolas, and represent the effect of the film while the area per molecule is greater than the cross-section of the chain or the head. The molecules of the film are under a vertical force due to the attraction of the polar group for the water, the force which causes orientation but is not sufficient to cause actual solution. The molecules of the film are furthermore held together by the attraction they have for one another. Counteracting this horizontal force is the kinetic energy of the molecules of the film in equilibrium with the thermal agitation of the water molecules. This tends to disperse the molecules and those at the edge of the film evaporate, as they are confined to the surface of the water by the attraction of the polar groups. Adam accounts for the portion, *bc*, of the curve in this way.

Adam observed a change of "state" to take place when the films were gradually heated. What occurs can best be explained by referring to Fig. 7. The curve shows what happened when a palmitic acid film, spread over a $N/100$ HCl solution, was warmed, the strip C′ in Fig. V being maintained in its zero position under a constant force of 1.4 dynes. At the lower temperatures the area 25.1×10^{-16} sq. cms., corresponding to the cross-section of the head, remained constant until between 28° and 35° a sharp expansion took place, followed by a small steady expansion above 35°. The expansion coefficient above this temperature corresponds in magnitude to the thermal expansion coefficient of a gas. A change of state evidently occurred, analogous to the change of solid to gas. The longer the carbon chain, the greater is the lateral attraction between the orientated molecules and, as a result, the temperature at which this change occurs rises with length of carbon chain. This is brought out by the last column of Table IV, an additional CH_2 group corresponding to a rise of 9°. That the polar group has an influence and that therefore its lateral attraction comes into play is shown by comparing stearic acid and stearic nitrile films, the temperature of change of state of these films differing by 20° although they have the same number of CH_2 groups per molecule. This shows the relatively great attraction between the polar groups as compared to the hydrocarbon chains.

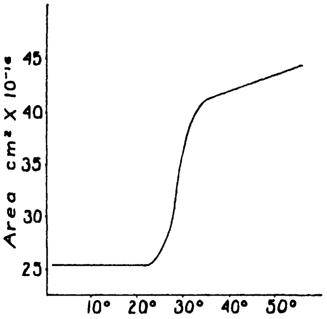

Fig. 7

The experiments described illustrate the existence of orientation of molecules and the predominating influence of the polar group on the properties of molecules.

Effect of Orientation on Physical Properties: In the preceding sections it was shown that molecular orientation exists under certain conditions and it is worth while to point out definitely what influence this phenomenon may be expected to have on the physical constants.

The magnitudes of the physical properties, melting point, surface tension, van der Waals' *a*, etc., are governed by the molecular forces. The larger the relative values of these constants the greater are the molecular forces. Melting point can be interpreted as the temperature at which the molecules are anchored to definite positions in space relative to one another, that is, the temperature at which the molecular force of attraction is strong enough to prevent translational and rotational movement due to their kinetic energy of the molecules.

Surface tension of a liquid is due to the differential force of attraction on the molecules near the surface of the liquid at low vapor pressures, there being a larger number of molecules below than above the surface layer. The critical temperature is the temperature at which the average kinetic energy of the molecules is just sufficient to permit their escape from the main body of the liquid under the condition of concentration least favorable for escape. Van der Waals' *a* is a measure of the difference of pressure registered on a manometer from the true pressure existing in the bulk of the gas.

In the following table a number of related compounds which have been examined are written down in a decreasing order of magnitude of the physical constants mentioned above. The substances chosen are compounds for which the constitutional formula is well known and (except in the case of the triple bond compounds) can be readily represented by the Lewis-Langmuir or Thomson atom.

TABLE V

Critical Temperature, Gases	Surface Tension, Liquids	Freezing Point, Solids
Ethyl alcohol	Ethylene oxide	Acetylene
Ethylene oxide	Acetaldehyde	Allylene
Acetaldehyde	Acetylene	Ethylene oxide
Methyl ether	Methyl ether	Ethyl alcohol
Allylene	Allylene	Acetaldehyde
Propane	Propylene	Methyl ether
Propylene	Propane	Ethylene
Acetylene	Ethylene	Ethane
Ethane	Ethyl alcohol	Propylene
Ethylene	Ethane	Propane

The order of the compounds is by no means the same in all three columns. If the properties are really representative of molecular force of attraction, the first conclusion would be that the force of attraction varies with the temperature, that is, with the molecular velocity. Although this is doubtless true to a certain extent, inasmuch as the violence of collision may influence the relative positions of the atoms in the molecule, there is another reason for the variation in the columns, namely, that the molecular force influences the molecules in two ways: first of all, the attraction of the centers of the molecules which tends to cause approach; secondly, the polarity of this force which tends to orientate the molecules relative to one another. In the case of gases, the first predominates, since, due to the equilibrium between rotational and translational energy, the rotation of the molecule may be looked upon as preventing orientation. This is not so in the case of the molecules in the surface of a liquid. Langmuir's ingenious experiments have shown that polar molecules at the surface of a liquid are, on the average, orientated so that the surface energies are representative of the attraction of the polar group for the main body of the molecules which are not orientated. This force diminishes with length of molecule or rather with the distance to which the polar group can get below the surface. In a solid, all molecules are so completely orientated that they lose their identity to such an extent that the solid as a whole may be regarded in many cases as one molecule; quite a different force will be required to pull the molecules into the liquid.

The critical temperature is, then, the measure of the attractive force between the molecules at the surface of a gas and the main body of the gas, neither set of molecules being orientated. The surface energy gives the force of attraction between the molecules at the surface, which are orientated, and the bulk of the molecules, which are not orientated. The melting point is a measure of the attraction between orientated molecules at the surface and the bulk of the molecules, which, in this case, are also orientated. Other physical properties similarly depend on one or other of the above possible orientation combinations. Thus, van der Waals' a and critical temperature, latent heat of evaporation and surface tension, are, in a broad sense, interchangeable in the above table.

In general though, taking a large number of different substances, those which come near the top in one list come near the top in another. This applies particularly to those which are not decidedly polar. The critical temperature and van der Waals' a are the best measure of the total attractive force.

Cohesive Force, Law of Force of Molecular Attraction: It has already been mentioned that liquids have a cohesive force evidenced experimentally by a tensile strength which cannot be measured quantitatively. It follows from the derivation of van der Waals' equation that the cohesive force is represented by $\frac{a}{v^2}$, where a is van der Waals' constant. When a is calculated for water from the critical constants of that substance, (and it must be remembered that a is obtained only approximately in this way), the surprisingly large value of eleven thousand atmospheres is obtained. This is called the "intrinsic pressure." A manometer of infinitely small thickness when placed in the water would register this pressure in addition to the comparatively insignificant vapor pressure. The pressure would be due to the attraction of the molecules on the opposite sides of the imaginary manometer. Since the molecular force of attraction falls off very rapidly with the distance, as is evidenced by the constant surface tension of a film down to a thickness of 10^{-6} cm., the manometer would have to be of a thickness less than this in order to indicate any intrinsic pressure whatever. Obviously, this pressure cannot be measured by means of a manometer. The illustration serves to show, however, what is meant by intrinsic pressure.

Stefan [1] and Dupré [2] have suggested methods for the indirect determination of intrinsic pressure. Dupré considers that the internal heat of vaporization of a liquid is a measure of the intrinsic pressure. Stefan has argued that the latent heat of vaporization of unit volume measures twice the intrinsic pressure. This would result from the conclusion that the work necessary to drag a molecule from the interior to the surface of a liquid is equal to that which would suffice to drag the molecule outwards from the surface beyond the range of molecular attraction. If this relation holds,

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[1] *Wied. Ann.*, **29**, 655 (1886).

[2] *Comptes Rendus*, **66**, 141 (1868).

$$\int_{v_l}^{v_g} \frac{a}{v^2}\,dv = \tfrac{1}{2}L_i.$$

From this equation putting dv equal to 1 cc., and assuming a value for the internal latent heat of vaporization for water equal to 540 cals., an intrinsic pressure of the order of ten thousand atmospheres is calculable. It should not be expected that such a calculation will give anything other than the order of magnitude, since additional degrees of freedom, more particularly of vibrational motion, may be gained by the molecules on evaporating.

In unassociated liquids where molecular regional orientation is assumed to be absent, the effective volume of a molecule may, owing to its rotation, be regarded as spherical. If the law of attraction has the form $\frac{C_1}{r^n}$, the work done in separating the molecules from their initial average distance r_l in the liquid, to their final average distance r_g in the gas will be

$$\int_{r_l}^{r_g} \frac{C_2}{r^n}\,dr = \frac{C_2}{n-1}\left(\frac{1}{r_l^{\,n-1}} - \frac{1}{r_g^{\,n-1}}\right).$$

J. W. Mellor[1] has pointed out that this is equal to

$$\int_{v_l}^{v_g} \frac{a}{v^2}\,dv = a\left(\frac{1}{v_l} - \frac{1}{v_g}\right).$$

Since v_l and v_g are proportional to r_l^3 and r_g^3, $(n - 1)$ will be equal to 3, and hence $n = 4$.

Unfortunately, from an experimental point of view the internal latent heat relationship would require L_i proportional to $\left(\frac{1}{v_l} - \frac{1}{v_g}\right)$, and this does not hold for any substance over a temperature range. Mills,[2] for instance, assuming that the force of attraction varies as the inverse square which would make the work done equal to $C_3\left(\frac{1}{r_l} - \frac{1}{r_g}\right)$, and, taking Dupré's idea that the work done in separating the molecules is equal to the internal latent heat, concluded that L_i would be proportional to $\left(\frac{1}{(v_l)^{1/3}} - \frac{1}{(v_g)^{1/3}}\right)$. He found that the experimental values of L_i, v_l, and v_g obeyed the above relationship for some thirty substances over a wide range of temperatures. Edser[3] in a recent paper has criticized these deductions on the ground that the variation of the constant with the temperature was neglected. He points out that the inverse square law obviously cannot hold and that the agreement obtained by Mills was due to the variation in molecular force of attraction with the temperature which just compensated for the error involved in using the inverse square law. Edser obtains empirically that a must be replaced by $a\left(1 - \frac{1}{2}\sqrt{\frac{T}{T_c}}\right)$, and comes to the conclusion that the intrinsic pressure is equal to $L_i\left(1 - \frac{1}{2}\sqrt{\frac{T}{T_c}}\right)$ which gives the value of the intrinsic pressure for water (which has been used above as an illustration) as twelve thousand atmospheres. In the same paper, Edser shows that the surface tension is equal to the intrinsic pressure multiplied by the diameter of the molecule and a known function of n where n is the power in the inverse distance law. By using the known values of the surface tension, the internal pressure given by the above equation, and an approximate value for the molecular diameter, sixty-five different substances gave the most probable value of n as being 8, so that the attraction apparently varies as the inverse 8th power. Space does not permit further discussion of the derivation of Edser's relationship between intrinsic pressure and surface tension.

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[1] *Phil. Mag.*, [6] 3, 423, 1902.

[2] Mills, *J. Phys. Chem.*, 6, 209 (1902); 13, 512 (1909).

[3] Fourth Report of British Association on Colloid Chem., p. 40 (1922).

The value $n = 8$ is not proven conclusively, as Edser himself emphasizes. The assumption which has to be made in calculating the diameter of the molecules and the assumption that the internal latent heat represents only the work done in separating the molecules from one another are not alone the causes of this uncertainty. The function of n is such that a large variation in n affects the relationship only slightly. Moreover, it is probable that n will vary from one species of molecule to another. But it does seem certain that n is equal to or greater than 4.

The range of molecular force is of course a subject of great importance and depends upon the value of C as well as on the value of n in $\frac{C}{r^n}$. The range given by the above expression is of course infinite, but may be arbitrarily defined as a distance at which it becomes negligible compared to the attractive force of gravity.

Viscosity of Liquids: The mean free path of a molecule, which, in the case of a gas, could be estimated so readily from viscosity and thermal conductivity data, can manifestly not be evaluated in the case of a molecule of a liquid. The mean free path of a molecule of a liquid is certainly very small relative to that of a molecule of a gas; possibly it differs so little from the average distance between the molecules that one hesitates to use the term at all when applied to liquids. Not only is the number of molecules per cubic centimeter enormously greater than in the case of a gas, but the molecular attractive forces play a greater part in deflecting the molecules and shortening their mean free path in this way. The phenomenon of diffusion is evidence of the existence of a mean free path, but no definite information can be obtained concerning the magnitude of the free path. For, the diffusion can at present only be followed by the movement of dissolved molecules and this introduces the complex problem of the attraction between solvent and solute molecules. Information on this question may be obtained in the future by measuring the rate of the diffusion of one radioactive isotope through another. As will be seen, the coefficient of viscosity throws no light upon the mean free path of a liquid molecule.

The coefficients of viscosities of liquids can be most conveniently determined by a method depending on the rate of flow through capillary tubes, making use of Poiseuille's relationship. The coefficients of viscosity show that there is a marked increase with increase in molecular weight. The temperature coefficient of viscosity of a liquid is opposite in sign to that of a gas.

The problem of viscosities of liquids was greatly clarified by the work of Phillips,[1] who measured the viscosity of carbon dioxide at various temperatures over a large range of pressures extending to very high pressures, where the carbon dioxide may be looked upon as being in the state of a liquid so far as the molecular forces of attraction are concerned. In Fig. 8 are shown the isobars of the coefficients of viscosity at various temperatures. The 1-atmosphere isobar shows that the viscosity increases with the temperature in accordance with the kinetic theory of gases. In the neighborhood of this pressure also, Maxwell's law, that the coefficient of viscosity does not vary with the pressure, holds fairly well. The law, however, only holds as long as the gas approximates to the ideal condition. As the pressure is increased considerably, new factors come into play and the viscosity increases with increase in pressure. The 40-atmosphere isobar still shows a positive but slightly smaller temperature coefficient for the viscosity. The 60-atmosphere isobar indicates that viscosity is independent of the temperature. At this pressure and over the temperature range shown, the average volume of the carbon dioxide is some twenty-five times that of the space occupied by the molecules as calculated from van der Waals' b. The 70-atmosphere and higher isobars show negative temperature coefficients similar to the temperature coefficients of viscosity of liquids. Thus, the change in the property of viscosity varies continuously from gas to liquid.

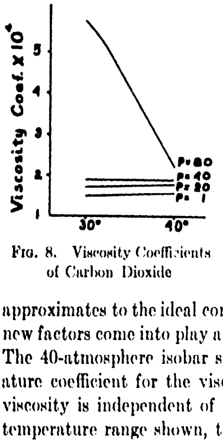

FIG. 8. Viscosity Coefficients of Carbon Dioxide

The motion of a stream of molecules through a region dense with other molecules means a displacement of these molecules. This can only be accomplished by their moving against the attractive forces existing between them. The motion is analogous to that of one piece of sandpaper moving over another against which it is pressed. The two pieces of paper will not be as close together as they are when at rest. Motion of the molecules through the other molecules of a compressed gas requires work to be done against the intrinsic pressure, and this factor will eventually outweigh all others. Hence, the viscosity of a gas is greatly increased when the intrinsic pressure becomes large. In a liquid, the intrinsic pressure is given by $\frac{a}{v^2}$ which, when the vapor pressure is low, is proportional to $\frac{1}{(v - b)}$ · The increase in volume of a liquid with temperature will therefore decrease the viscosity. Batschinski[1] has shown that the viscosity of a liquid is closely related to its volume when examined over a temperature range.

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[1] *Proc. Roy. Soc.*, **87A**, 48 (1912).

Specific Heats of Liquids: The molecular heats of liquids cannot, as yet, be deduced from theoretical principles. The heat added to a liquid is used up in so many different ways, few of which can be separately estimated, that this inability to calculate the molecular heats of liquids is not surprising. Energy has to be supplied not only to increase the translational and rotational movement of the molecules but also to increase the vibrational movement of the atoms in the molecules. The latter is quite marked as evidenced by the increased molecular heat with increased number of atoms in the molecule. A fairly constant increase in molecular heat per additional CH_2 group in homologous series has been found. Besides these modes of energy consumption, heat is required for expansion against the molecular forces of attraction which, in a liquid, are considerable. The specific heats of substances in the liquid state are, consequently, greater than those of substances in the solid or gaseous states.

The specific heats of liquids have been measured at constant pressures only, since the determination at constant volume presents great experimental difficulties. The molecular heat at constant pressure for a polyatomic gas is of the order of 5 to 10 calories. Compare this with the molecular heat of the liquid hydrocarbon, mesitylene 1-3-5 $C_6H_3(CH_3)_3$, which is 76.4 cal. The molecular heat of an organic liquid increases from 6 to 10 calories for the addition of each CH_2 group. This fact is the best evidence for the large amount of energy bound up in the vibratory motion of the atoms in the molecule. It is therefore not surprising that the molecular heats of liquids increase with rise in temperature just as do the molecular heats of gases with vibrating atoms. The molecular heats of liquids containing only one atom to the molecule might be expected to be relatively low. They should not increase with the temperature since there is no possibility of increased vibratory motion of atoms in the molecule. As a matter of fact one would expect a negative temperature coefficient for the molecular heat of a monatomic liquid. The heat added to a monatomic liquid should be 5 cal. plus the heat equivalent of the work done during expansion, that is, the work done in separating the mo'ecules against their molecular attractions. With rise in temperature and therefore increased volume this work should be less and less and therefore the specific heat should diminish. Two liquids believed to be monatomic have so far been examined. Liquid argon has a molecular heat of 10.5 cal., constant over the short temperature range of sixteen degrees over which measurements have been made. Mercury has a molecular heat of 6.68 cal.[1] at 0° C. and this actually decreases to 6.56 cal. at 85° C., in conformity with the idea outlined above.

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[1] *Z. physik. Chem.*, **37**, 214 (1901).

The proper procedure in an examination of the molecular heats of liquids would be to measure the specific heats of gases under increasing degrees of compression and to follow out the changes in specific heat as the gas is compressed from a condition in which it is in its ideal state to pressures where its condition approaches that of a liquid.

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[1] Barnes and Cooke, *Phys. Rev.*, **16**, 65 (1903).

CHAPTER V

THE SOLID STATE OF AGGREGATION

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The ordinary conception of a solid represents it as a portion of matter possessing rigidity—that is, offering resistance to forces tending to deform it. Solids differ from fluids in not being subject to flow. Such a distinction has little value from the scientific standpoint because of its indefiniteness; for flow can be induced in nearly any solid by the proper application of a sufficiently great force. A much more fundamental distinction among the states of matter follows from the recognition of the fact that the majority of substances can exist in solid forms which are bounded by plane surfaces so oriented to one another that the whole possesses some degree of symmetry. A substance in this state is said to be crystalline and the state is called the crystalline state of aggregation. All other solid bodies are classed as amorphous and are to be regarded as nothing other than liquids of great viscosity. Among such substances are glasses and resins.

That amorphous solids differ from liquids only in degree is demonstrated by the fact that on heating they lose, by imperceptible gradations, their rigidity and may become as fluid as water. The absence of a definite transition point renders it futile to attempt to distinguish such bodies as solid under one set of conditions and liquid under another. With crystalline solids, however, matters are very different. Every crystalline solid has a definite transition point at which it undergoes an abrupt change into a liquid with absorption of heat. Amorphous solids can be regarded as partaking in that continuity of state which characterizes the transition from gas to liquid under given conditions. No such continuity characterizes the transition from crystalline to liquid states, so far as can be discovered. Investigations on the influence of tremendous pressure on the behaviors of crystalline substances have shown that the transition to the liquid state invariably takes place abruptly when a definite temperature, which depends upon the pressure, is reached.[1]

It may therefore be concluded that there is a fundamental difference between the crystalline and all other states of aggregation. From comparatively early times it has been believed that crystals are to be regarded as structures built up by the symmetrical arrangements of some ultimate units, as contrasted with the random arrangement of such units in fluids. The discovery by Friedrich and Knipping,[2] acting on a suggestion of Laue,[2] that crystals act as three-dimensional optical gratings for X-rays, with all its results, has left little doubt that such is the case. The constituent atoms in a crystal are arranged in a definite pattern which is regularly repeated throughout the body of the crystal. In fluids, definite arrangements of atoms within the molecules undoubtedly persist, as witness the fact that liquids and vapors may be optically active, but the molecules themselves are distributed at random.[1]

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[1] See, e.g., Bridgman, *Proc. Am. Acad. Sci.*, **47**, 441 (1912).

[2] *Sitzber. K. Bay. Akad.*, June (1912). *Jahrbuch. d. Radioakt. u. Elektronik*, **11**, 308 (1914).

The Elements of Crystallography

Crystal Form: A study of the forms which crystals assume has led to the recognition of certain general laws of crystal form and to a classification on the basis of the degree of symmetry possessed by such forms. This is embodied in the science of crystallography.

If different crystals of some pure substance which have been prepared by essentially similar processes are examined, they will be found to differ as to size and as to the extent of development of corresponding faces. These things depend, in a manner only incompletely known, upon the method of preparation. If, however, the angles formed by the intersection of corresponding faces on these different crystals are measured, it is found that these are always the same. This fact is embodied in the first law of crystallography—the law of the constancy of interfacial angles.

Even a cursory examination of a crystal is in many cases sufficient to convince one that the orientation of its faces is by no means random. Thus, the faces on crystals of sodium chloride obviously unite to form a cube. In the majority of cases, however, there are clearly present faces of different characters. These usually occur in groups of like faces arranged symmetrically with respect to the crystal as a whole. Such groups constitute a form.

The second law of crystallography deals with the orientation of the faces on a crystal with respect to one another. The crystal may be supposed to have running through it axes (known as axes of reference) with respect to which the faces may be placed in space. When these are suitably chosen, it is found that all faces cut a given axis at distances from the origin which stand to one another as small whole numbers, if they cut that axis at all for they may alternatively be parallel to it. This is the second law of crystallography—the law of rationality of intercepts or indices.

It follows from the law of rationality of intercepts that there corresponds to each reference axis in a given crystal an indivisible unit of length in terms of which the intercepts of faces on that axis are expressible as small whole numbers. This unit may or may not be the same for the different axes of the crystal. The actual values of the unit for corresponding axes on individual crystals obviously depend upon the size of the crystals. The *ratios* of the units on the different axes are always the same for crystals of the same substances, however. This follows from the law of constancy of interfacial angles and is sometimes termed the law of constancy of axial ratios.

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[1] See however liquid crystals and surface films.

For the axial ratios of a crystal, it is customary to choose the ratios of the intercepts of some characteristic face rather than the ratios of the above-mentioned units, some one intercept being taken as unity. The intercepts of all other faces can then be simply related to these. For example, in the mineral, barite, a face whose intercepts stand in the ratios 0.815 : 1 : 1.313 is chosen as the unit face. We may designate these as $a : b : c$. The symbols of all other faces can then be written in terms of these. Two such faces have intercepts which stand in the ratios 1.630 : 1 : 1.313 and 0.815 : ∞ : 0.328, respectively. These can evidently be written as $2a : b : c$ and $a : \infty b : \frac{1}{4}c$. The latter are known as the *Weiss symbols* of the faces. As these symbols are rather cumbersome, another set, in which the smallest whole numbers expressing the *ratios of the reciprocals of the coefficients* of the Weiss symbols, is now universally used. These symbols are known as the *Miller indices* of the face. Thus, for the second of the two faces mentioned above, the Weiss symbols are $a : \infty b : \frac{1}{4}c$. The coefficients stand as $1 : \infty : \frac{1}{4}$. The reciprocals of these stand as 1 : 0 : 4. The Miller indices of the face are expressed as [104]. For the other face, the Miller indices are [122].

The Classification of Crystals: There are recognizable, on the majority of crystals, sets of faces similarly oriented with respect to the symmetry of the whole. Such a set is known as a *form*. Thus, the six faces of a cube together constitute a form, as do the eight faces of an octahedron. These forms can be gathered into groups which have the same number of axes and planes—that is, the same elements—of symmetry. Such groups constitute the crystal classes, of which there are 32. Axes of reference may be chosen for each of these classes such that the indices of all the faces of any one form are the same. When this is done, it is found that the crystal classes can be grouped into sets for which the axes are the same as regards equality or inequality of their lengths and of the angles they make with one another. These sets are the crystal systems, of which there are seven. These seven crystal systems with their axes are:

I. *The Triclinic or Anorthic System* Three axes of unequal length all inclined at unequal angles other than 90°, 60°, 45° or 30°.

II. *The Monoclinic or Monosymmetric System* Three axes of unequal length, one at right angles to the other two, which are inclined to one another.

III. *The Rhombic or Orthorhombic System.* Three axes of unequal length but at right angles.

IV. *The Tetragonal System* Three rectangular axes, two of which are of equal length.

V. *The Trigonal System:* Three axes of equal length, forming equal angles (other than 90°) with one another.

VI. *The Hexagonal System:* Three axes of equal length lying in the same plane and inclined at 60° to each other and a fourth axis perpendicular to them and unequal to them in length.

VII. *The Cubic System:* Three equal rectangular axes.

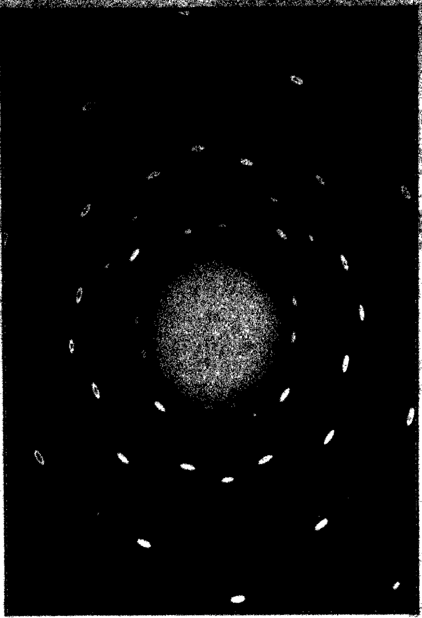
Crystal Structure

It was early recognized that the external form of crystals and their properties of cleavage indicated an internal structure consisting of some regular arrangements of ultimate units in space. Haüy, the discoverer of the law of rational indices, laid stress on the fact that when crystals of many substances, such as calcite and rock salt, are shattered, the fragments have the same form as the original crystals, and suggested that repetition of the process of fragmentation would eventually yield elementary particles (molecules integrantes) having the same form as the larger crystals. These elementary particles were regarded by Haüy as the "bricks" which form the complete crystal when packed side by side. He was able to show that this type of structure would account for the law of rational indices. Although this particular theory became somewhat discredited for many reasons, the fundamental idea has been retained. By degrees, however, the emphasis has been shifted from the elementary particle itself to its center of gravity or other point chosen the same for all the particles. These points can be thought of as arranged in some regular fashion on a three-dimensional trellis-work. Suppose that three sets of parallel planes interpenetrate, the distances between planes being the same in each set but in general different for the different sets. Then the lines in which the sets of planes, taken in pairs, intersect, represent the trellis-work and the points at which one plane of each of the three sets intersect, represent the points at which the elementary particles may be placed. Such an arrangement is known as a *space-lattice.*

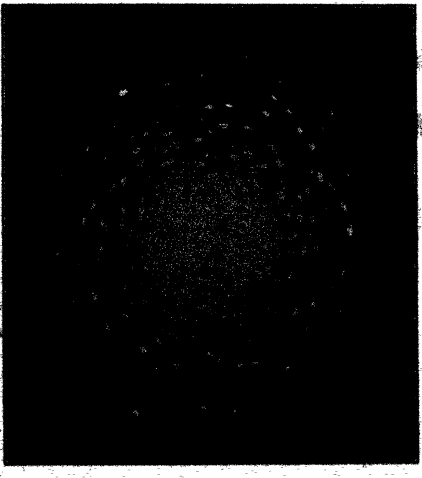
It is evident that as many interpenetrating space-lattices could be drawn as there are like points in the elementary particles. For example, one such lattice might be constructed for each atom in the molecule. Thus, if in calcite, the molecule $CaCO_3$ is taken as the elementary particle, five interpenetrating space-lattices of identical dimensions could be constructed, at the points of one of which would be placed the calcium atoms, of another the carbon atoms and of three others the three oxygen atoms. These five lattices may be regarded as derived from the fundamental lattice by translation. A new and more complicated arrangement of points in space obviously results. Such an arrangement of points is known as a *space-group.*

From considerations of symmetry, it has been found that only a restricted number of space-groups, obeying the law of rational indices, is possible. There are in fact just 230 such symmetrical arrangements of points in space. With respect to their symmetry, these 230 arrangements fall naturally into 32 classes which are identical with the 32 crystal classes. If the space-groups represent the actual grouping of atoms in crystals, it is obvious that there are many such groupings possible in the majority of the crystal classes, that is, there are a number of alternative arrangements of atoms which all have the same symmetry. The older method of studying crystals, based on the character of the faces developed, can usually establish the symmetry and therefore the class to which a crystal belongs, but gives no information as to the space-group, and therefore the actual arrangement of atoms. It is the great achievement of the X-ray method of analysis of crystal structure, which will now be discussed, that it was able to take this last step. By means of X-ray analysis, the arrangements of atoms in a large number of crystals have now been definitely established.

PLATE I



(*a*) Laue diagram of magnesium oxide



(*b*) Laue diagram of potash alum

TYPICAL LAUE DIAGRAMS

Diagrams by courtesy of Dr. R. W. G. Wyckoff.

X-rays and Crystal Structure: The investigations which have culminated in the determination of the arrangements of atoms in crystals with the help of X-rays had their beginning in attempts to obtain diffraction effects with X-rays. With an ordinary optical grating, there is no measurable diffraction, indicating that if X-rays are actually light waves, their wave-lengths must be very small even compared to that of visible light.[1] Various estimates had set these at 10^{-8} to 10^{-9} cm. Since the spacing of the lines of a grating must be of the same order as the wave-length of the light to be measured in order to obtain appreciable diffraction effects, it would obviously be impossible to prepare a grating which would diffract X-rays if their wave-lengths are as estimated, because the distance between lines would need to be comparable to the distances between the molecules of the solid.

It was suggested by Laue[2] (1912) that if crystals in reality represent orderly arrangements of atoms or molecules, they should act as three-dimensional optical gratings for X-rays, since various estimates had placed the distances between atoms in crystals at about 10^{-8} cm The determination of the type of spectrum to be expected offered considerable difficulties, but Laue was able to show that if a beam of X-rays was thrown upon a crystal, it should be partially converted upon transmission through the crystal into a number of diffracted beams arranged symmetrically around the primary beam in a manner governed principally by the symmetry of the crystal. This should be revealed on a photographic plate, placed directly back of the crystal, by a central image surrounded by a symmetrical group of spots. Experiments, carried out by Friedrich and Knipping[3] soon after, completely confirmed the prediction. Two so-called Laue photographs of the diffraction patterns so obtained are shown in Plate 1.

This discovery not only demonstrated that X-rays were in reality light of short wave-length but also indicated that information as to the actual arrangements of the atoms or molecules in crystals could probably be obtained by this method. Because of the difficulty of the analysis and the almost complete lack of information as to the characteristics of either the X-rays or the atomic arrangements in the crystals, little use could be made of the results at the time.

The Bragg Method of X-ray Analysis: W. H and W. L. Bragg[4] shortly afterwards devised a modification of the Laue method which first made possible direct determinations not only of the actual arrangements of atoms in many crystals but also provided a method of determining the absolute wave-lengths of X-rays.

The space-lattice arrangement of atoms or molecules in a crystal indicates that the atoms or molecules can be regarded as occurring in parallel planes whose orientations are fixed by the law of rational indices and by the symmetry of the crystal. Each face of a crystal is developed parallel to some one of these planes and the most frequently occurring faces are usually developed parallel to those planes which are richest in atoms or molecules, which are those planes of small indices. The Braggs were able to show that the diffraction of X-rays by a crystal could be just as satisfactorily and much more simply treated as reflections from these successive planes of atoms rather than as diffractions from a three-dimensional grating in which each atom represented a center of diffraction. In the Bragg method, X-rays composed principally of a single wave-length (i.e., "monochromatic" X-rays) are allowed to fall on a face of a crystal. A reflection spectrum is obtained, that is, the monochromatic light is "reflected" at certain definite angles only. This is analogous to the reflection of visible monochromatic light by a stack of very thin plates of glass. The values of these angles vary with the angle of incidence of the beam, other things being equal. The problem is considerably simplified if only those cases are considered when the beam is "reflected" at an angle equal to the angle of incidence. Under these conditions, a very simple relationship exists between this angle, the distance between successive parallel planes and the wave-length of the X-rays.

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[1] The wave-length of sodium – *D* line is 5896×10^{-8} cm.

[2] *Sitzber. K. Bay. Akad.*, June (1912). *Jahrbuch d. Radioakt u. Elektronik*, **11**, 308 (1914).

[3] *Sitzber. K. Bay. Akad.*, June (1912).

[4] X Rays and Crystal Structure, by W. H and W L. Bragg, 1915. See also W. H. Bragg, *J. Chem. Soc.*, **109**, 260 (1916).

In Fig. 2, *p*, *p* · · · are supposed to represent such planes parallel to some face of a crystal. Their common spacing is equal to *d*. $AA'A''A'''$ represents an advancing wave front of X-rays of wave-length $\lambda(AA_1)$. Consider those parts of this beam of X-rays which unite to give a reflection along BC. The distances traveled by different parts of the beam in going from $AA'A''A'''$ to C differ according as they are reflected from one or another plane. Thus, considering only the first two planes, the paths are ABC and $A'B'C'$, respectively. The different parts of the beam, which are originally in phase, will not be in phase when they reach C, due to the difference in path, unless this difference is a whole number of wave-lengths. Except when this is the case, there will be no reflection at C, for the cumulative effect of even a slight difference in path between waves reflected by successive planes is sufficient to cause almost complete interference. The difference in path depends upon the value of the angle θ, other things being equal. Hence it is necessary to determine for what value of θ the difference in path is numerically equal to a whole number of wave-lengths.

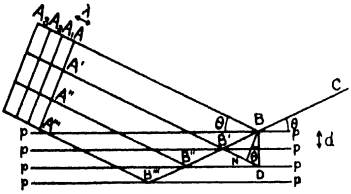

Fig. 2

Extend $A'B'$ to D and draw BD (which is perpendicular to the planes *p*, *p* · · ·). Draw BN perpendicular to $A'D$. The difference in length of the two paths ABC and $A'B'C$ is equal to

$$BB' - B'N = \Delta.$$

But

$$BB' = B'D.$$

Hence

$$B'D - B'N = ND = \Delta.$$

$$\frac{ND}{BD} = \sin \angle NBD.$$

But

$BD = 2d$, and $\angle NBD = \theta$, the angle of incidence.

Hence

$$ND = \Delta = 2d \cdot \sin \theta.$$

Maxima in reflection will occur when Δ ($= ND$) is equal to a whole number of wave-lengths, that is, to $n\lambda$, where n is a whole number. Hence, for this condition we have,

$$n\lambda = 2d \sin \theta.$$

The apparatus used by the Braggs (Fig. 3) is similar to a spectrometer (and is in fact used as such). In place of an ordinary grating, the crystal is mounted at the center of a turn-table having a graduated circle, with the face of the crystal normal to the table. X-rays from a suitable source are passed through absorbing screens to render them as nearly monochromatic as possible and then through two adjustable lead slits to obtain a well-defined beam. This beam is adjusted to strike the center of the crystal face, which is set on the axis of the turn-table in order that rotation of the turn-table will not throw it out of alignment The reflected rays are received in an ionization chamber mounted on an adjustable arm whose pos-

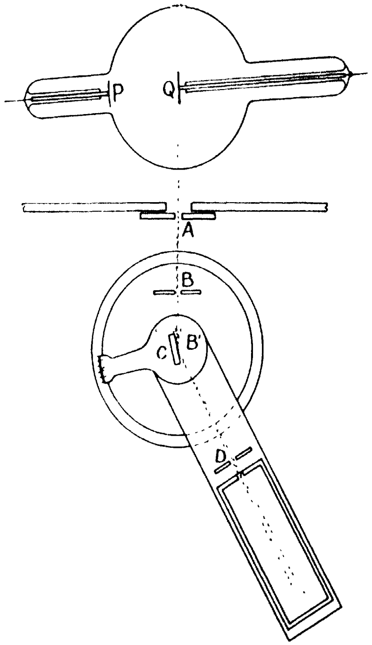

FIG. 3. Bragg's X-ray Spectrometer

tion relative to the crystal face can be read from a second graduated circle. The ionization chamber contains some gas such as SO_2, which is easily ionized by X-rays, and is in connection with an electroscope, by means of which the intensity of the ionization and hence of the reflected X-rays can be determined. The crystal face and the ionization chamber are rotated about their common axis, keeping the angle between the face and the ionization chamber the same as that between the face and the incident beam,[1] and the strength of the ionization produced by the X-rays at different settings is measured. The settings corresponding to the maxima in reflecting power are thus determined. The corresponding angles between the face and the incident beam are those which should satisfy the relation,

$$n\lambda = 2d \sin \theta.$$

Since d and λ should be constant for any particular face and type of X-rays, it is evident that the values of $\sin \theta$ should stand in the ratio of small whole numbers corresponding to the integral values of n.

$$\text{Sin } \theta = \frac{n\lambda}{2d} = nk$$

where k is a constant. This is found to be the case. Measurements on the cube face of NaCl gave maximum reflections at $\theta = 5.9°$, $11.85°$ and $18.15°$, using X-rays from a palladium anticathode. The values of the sines of these angles are 0.103, 0.205 and 0.312, respectively, numbers which stand in the ratio of 1 : 2.00 : 3.03 or nearly 1 : 2 : 3, as was to be expected. From the above, the spacing of planes parallel to the cube face can be obtained in terms of λ, since the value of $\sin \theta$ for a given value of n is known. Thus, in the above example, the value of d is

$$d = \frac{n\lambda}{2 \sin \theta} = \frac{1}{2(0.103)} \lambda = 4.85\lambda.$$

The analysis of crystal structure by the Bragg method consists in determining, by the means just outlined, the relative spacing of planes perpendicular to the principal directions through the crystal, by obtaining reflections of X-rays from the corresponding faces. These faces may be either those naturally occurring or ground on the crystal for this purpose. These relative spacings depend upon the arrangements of the structural units, that is, upon the fundamental space-lattices characteristic of each crystal system. If, therefore, the system to which the crystal belongs is known, the relative spacings to be expected for the different types of space-lattice possible can be calculated and compared with those found by X-ray analysis. Once the correct space-lattice has been determined, the absolute value of the spacing of the planes can be determined with the help of the density of the crystal and the Avogadro number (6.06×10^{23}). Knowing this, it is easy to calculate the value of λ; that is, the crystal can then be used as a reflection grating for the determination of the wave-length of X-rays.

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[1] This involves rotating the chamber through twice the angle of rotation of the crystal face.

The Crystal Structures of Sodium and Potassium Chlorides: The first crystals successfully studied by the Braggs were those of sodium and potassium chlorides. These both crystallize in the cubic system. There are three fundamental space-lattices possible to the cubic system. These are known as the simple cubic, the face-centered cubic and the body-centered cubic lattices. The whole space-lattice may be thought of as made up of a number of cells, among which the structural units of the crystal are distributed. Diagrams of such cells for the three cubic lattices are shown in Fig. 4. In the simple cubic lattice, one structural unit is associated with each corner of the cubic cell. In the face-centered cubic lattice, one unit is associated with each corner of the cell and one with the center of each face. In the body-centered cubic lattice, one unit is associated with each corner of the cell and one with the center of the cell. We may calculate the relative spacing of the planes containing these units in planes parallel to the cube face, perpendicular to the face diagonal and perpendicular to the cube diagonal for the three types of lattice. Such planes are possible crystal faces and have the Miller indices (100), (110) and (111), respectively. The faces of the first type would be cube faces; of the second, faces of a dodecahedron; and of the third, faces of an octahedron. Their relative spacings for the three types of lattice are given below, that of the (100) planes being taken as unity.

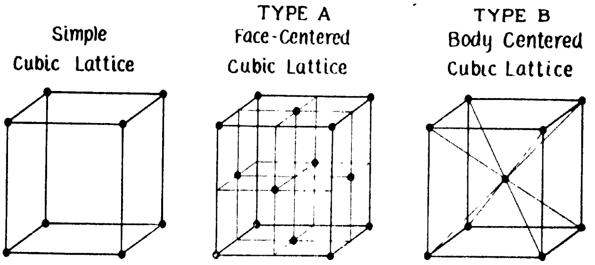

FIG. 4 Cubic Lattices

	(100)	(110)	(111)
Simple cubic	1	: $\frac{\sqrt{2}}{2}$	: $\frac{\sqrt{3}}{3}$
Face-centered cubic	1	: $\frac{\sqrt{2}}{2}$	: $\frac{2\sqrt{3}}{3}$
Body-centered cubic	1	: $\sqrt{2}$	: $\frac{\sqrt{3}}{3}$

The positions of the maximum reflections from the (100), (110) and (111) faces of crystals of sodium chloride with palladium X-rays are shown in Fig. 5. The height of the lines indicates the intensity of the reflections. The first-order reflections occur at 5.9°, 8.4° and 5.2°, respectively, for the three faces. (The last, from the (111) face, is abnormally weak. The probable reason for this will be given later.) The sines of these angles are 0.103, 0.146 and 0.094, numbers which stand in the ratio of 1 : 1.42 : 0.91. Since

$$d = \frac{n\lambda}{2 \sin \theta},$$

the corresponding values of d should be in the ratios of the reciprocals of these numbers, which are 1 : 0.71 : 1.10. The ratios of d for the three faces in the face-centered arrangement are 1 : 0.71 : 1.15. The agreement indicates that the fundamental lattice is the face-centered.

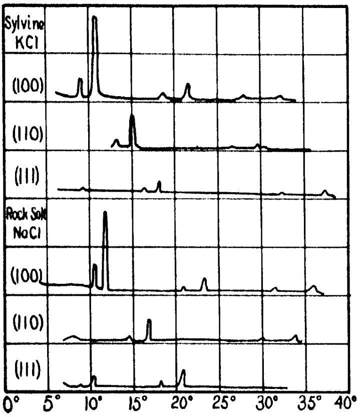

FIG. 5. Intensity of Reflections and Angle of Setting of Ionization Chamber

In the introduction to this section it was stated that we may associate with the points of the space-lattice the centers of gravity of the units of structure of the crystal or, if we wish, the atomic centers of any one kind of atom. Thus, if the structural unit in the sodium chloride crystal is the molecule NaCl, we may, if we wish, associate the centers of the chlorine atoms with the points of the fundamental lattice. Then, the centers of the sodium atoms will lie at the points of another lattice, identical with the fundamental one in dimensions but displaced from it in some direction, the two interpenetrating. Knowing that the fundamental lattice in a sodium chloride crystal is face-centered cubic, the problem of determining how the two lattices are oriented to one another is presented. It is known that the scattering power of atoms of a substance increases with the atomic weight. The X-ray reflections are due to scattering and since the chlorine atom is one and a half times as heavy as the sodium atom, it is probable that the reflections are mainly due to the chlorine atom lattice, though these will be altered somewhat by the presence of the sodium atom lattice. The only peculiarity noticeable in the sodium chloride X-ray spectrum is that the first order reflection from the (111) face appears to be abnormally weak and the third order spectrum is missing.

Suppose that the space-lattice carrying the sodium atoms is displaced from the fundamental space-lattice of chlorine atoms along the side of the fundamental cube half the length of the cube side. The effect of this will be to alternate sodium and chlorine atoms along each cube edge and give a "checkerboard" arrangement of atoms on the cube face. Such an arrangement, which is identical with the simple cubic arrangement except for the fact that it contains two kinds of atoms, is shown in Fig. 6, Type C. With this arrangement, the planes parallel to the cube faces contain both sodium and chlorine atoms in equal number and the spacing of these planes is the same as that of the fundamental face-centered lattice. The same is true of the planes parallel to the dodecahedral (110) faces. This arrangement will, however, bring planes containing only sodium atoms half-way between the (111) faces of the fundamental lattice. These planes must influence the reflections from the (111) faces. They would do so in the following manner. When the difference in path between waves reflected from two successive chlorine planes is equal to one wave-length, the difference of path between waves reflected from the sodium plane spaced half-way between and those reflected from either chlorine plane will be one-half a wave-length and therefore the two will be 180° out of phase. If the intensity of reflection from the sodium planes were exactly the same as that from the chlorine planes, there would therefore be no reflection whatever at the corresponding angle. If the reflection from the sodium plane is somewhat the weaker, the reflections from the chlorine planes will still be detectable but will be abnormally weak. This is what is found for the first order reflection from the (111) face of sodium chloride. The same will hold true for the third order reflection, when the waves from the sodium planes reach the ionization chamber $1\frac{1}{2}$ wave-lengths behind those from the chlorine planes. For the second order reflection the waves from the sodium planes are a full wave-length behind those from the chlorine planes and hence amplify the latter. The spectra are therefore what would be expected from this simple cubic type of lattice.

When a crystal of potassium chloride is examined, the spectrum (Fig. 5) is found to be of the same kind as that from sodium chloride except that the first order spectrum from the (111) face is completely lost. The arrangement of atoms is almost certainly the same as in sodium chloride but in this case the two kinds of atoms, potassium and chlorine, are of nearly the same mass and therefore reflect X-rays with so nearly the same intensity that the waves from the (111) potassium planes completely destroy those from the chlorine planes when the two sets are 180° out of phase.

The particular simple cubic or "sodium chloride" arrangement of atoms in sodium and potassium chlorides is therefore capable of accounting for the results. This, of course, does not eliminate the possibility of some other arrangement doing as well. This is very doubtful, however. An exhaustive investigation by Wyckoff[1] of such possibilities in the case of magnesium oxide, which also apparently has the "sodium chloride" arrangement, indicates that no other simple arrangement will account for the results.

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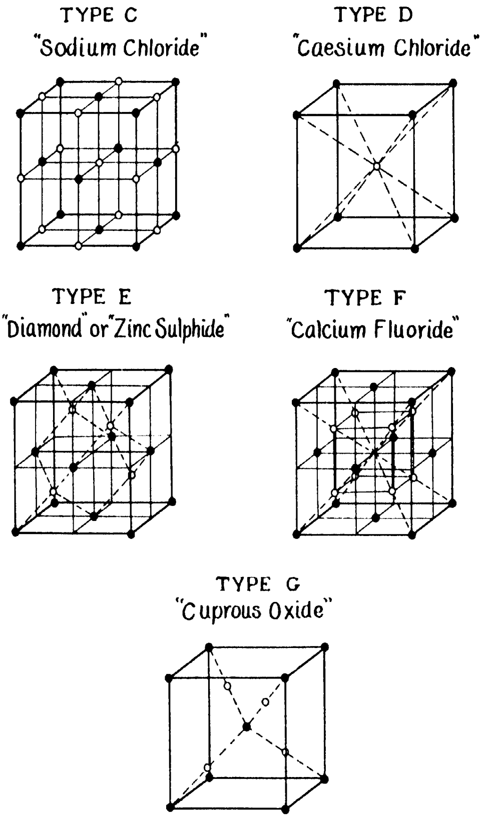
[1] For an extensive bibliography and discussion of X-ray data concerning crystals see Wyckoff, *J. Franklin Inst.*, **195**, 183, 349, 531 (1923).

Granting that the simple cubic arrangement is correct, it is possible to calculate the distances between planes and hence to determine the wave-lengths of the X-rays used. We first wish to know the side-length of the elementary cubic cell. The first step is to determine the mass of substance, say sodium chloride, which is associated with each cell. The elementary cell has a chlorine atom at each cube corner and one at the center of each face. Since each atom at a cube corner is also associated with seven other cubes, only 1/8 of its mass can be associated with the cube considered. But there are eight such atoms. Hence these altogether contribute the mass of one atom to the unit cell. Each


TYPE C "Sodium Chloride"

TYPE D "Caesium Chloride"

TYPE E "Diamond" or "Zinc Sulphide"

TYPE F "Calcium Fluoride"

TYPE G "Cuprous Oxide"

FIG. 6

atom in a cube face is associated with the adjacent cube and hence contributes only half its mass to the cube in question. The six such atoms altogether contribute the mass of three atoms to the cube. The total mass of chlorine to be associated with the unit cell is therefore equal to that of four chlorine atoms. Similarly it can be shown that four sodium atoms are to be associated with the cell. We may therefore say that the cell contains four molecules of sodium chloride. Now a gram molecule of sodium chloride occupies a volume of 27.0 cc. and contains 6.06×10^{23} molecules. The volume associated with four molecules is therefore

$$4 \times \frac{27.0}{6.06 \times 10^{23}} = 178 \times 10^{-24} \text{ cc.}$$

This is the volume of the unit cubic cell. The length of side of this cell is equal to the cube root of this number, which is 5.62×10^{-8} cm. Since one Ångstrom (Å.) is equal to 10^{-8} cm., this is 5.62 Å. The distances between planes parallel to a (100) face is equal to one-half of this value, or 2.81 Å. Having obtained a value for d_{100}, λ can be calculated. Using rays from a palladium anticathode, it was found that, for sodium chloride, $d_{100} = 4.85\lambda$, whence

$$\lambda = \frac{d_{100}}{4.85} = \frac{2.81}{4.85} = 0.58 \text{ Å}.$$

This is the wave-length of the characteristic X-rays from palladium. It is clear that by means of this method a crystal can be used to determine the wave-lengths of X-rays in a manner analogous to the determination of the wave-lengths of visible light with an optical grating. This is in fact the method by which the absolute wave-lengths of X-rays are calculated.

Having shown in the case of sodium and potassium chlorides how the crystal structure was worked out, it remains to set forth some of the principal results as to the crystal structures of substances which have followed from the investigation. First, however, brief mention will be made of an alternative method of procedure.

The Powder Method of X-ray Analysis: The Bragg method of X-ray analysis requires a well-developed crystal of moderately large size. There is another way in which well-defined diffraction effects can be obtained from crystalline substances. This method, which was published almost simultaneously by A. W. Hull[1] in the United States and by Debye and Scherrer[2] in Germany, depends upon the reflection of X-rays from the faces of minute crystals present in a crystal powder. All the important faces are apparently present on the various fragments of crystals in such a powder and these are oriented in all directions. If a beam of homogeneous X-rays is directed on to these, some will be oriented so as to allow of reflection, that is, so that the relation

$$n\lambda = 2d \sin \theta$$

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[1] *Phys. Rev.*, **10**, 661 (1917).

[2] *Physikal. Z.*, **17**, 277 (1916); *ibid.*, **18**, 291 (1917).

is satisfied. These reflections are registered on a strip of photographic film placed on a semicircle with the powder at its center. Such a film shows after exposure and development a number of fine lines which correspond to the reflection maxima. By comparing the arrangement of lines with what would be expected for different arrangements of atoms, the particular arrangement in crystals of the substance under examination can be determined.

The powder method has been of particular value in determining the crystal structures of the metals, which cannot readily be obtained in the form of large crystals.

The Powder Method as a Method of Chemical Analysis: In the powder method of X-ray analysis of crystal structure, a series of sharp lines, corresponding to the reflections from the various faces when the relation

$$n\lambda = 2d \sin \theta$$

is satisfied, are recorded on a strip of photographic film. These constitute a pattern which is unique for every substance. It has been shown by Hull[1] that this fact can be utilized in the qualitative analysis of substances in the solid state. For example, suppose that an ordinary chemical analysis in the wet way shows that a sample of crystalline solid in the form of small crystals contains Na, K, Cl and Br and it is desired to know what particular salts are present in the solid, whether NaCl and KBr or NaBr and KCl or all four. Ordinary analysis would be unable to show. If, however, the sample is ground to a powder and an X-ray photograph taken by the powder method, this will be immediately revealed, since each type of crystal lattice present will record on the photographic film its particular set of lines, which can then be identified by comparison with photographs obtained with the pure salts. From the relative intensities of the lines corresponding to the different substances, a rough quantitative estimate of the amount of each present can even be made.

Some Results of X-ray Analysis of Crystal Structure: The crystal structures of a relatively large number of substances crystallizing in the cubic system have been determined. Several types of arrangements of atoms are met with, drawings of which are shown in Figs. 4, 5 and 6.

Type A is the face-centered cubic lattice (see Fig. 4). This is the structure of a large number of metals. It represents one type of arrangement which would result from the closest packing of spheres. An alternative arrangement resulting in a hexagonal structure is also met with and is described below. In both, each atom is equidistant from 12 others.

Type B is the body-centered cubic lattice (see Fig. 4). This is the structure of many of the metals. Each atom is equidistant from eight others.

Type C is known as the simple cubic or "sodium chloride" arrangement. This is the structure of the alkali halides (except the cæsium salts) and the alkaline earth oxides and sulphides. The two kinds of atoms are arranged on two face-centered lattices which interpenetrate in such a manner that they combine to give a simple cubic lattice.

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[1] *J. Am. Chem. Soc.*, **41**, 1168 (1919).

Type D is known as the "cæsium chloride" arrangement. This is the structure of the cæsium halides, thallium chloride and the low temperature modifications of ammonium chloride and bromide. The two kinds of atoms are arranged on two simple cubic lattices which interpenetrate so as to bring the atoms of one kind at the centers of the cubes formed by the atoms of the other kind. The result is a body-centered lattice.

Type E is the "diamond" or "zinc sulphide" arrangement. It is based on a face-centered cubic lattice and represents the arrangement of atoms in the diamond and in silicon, germanium and grey tin. Many binary salts including zinc sulphide have the same type of lattice, the atoms of one kind occupying the positions at the corners and face centers of the cube and those of the other kind being at the centers of the alternate small cubes into which the face-centered arrangement can be divided. In crystals of diamond and of the other elements having this arrangement, the atoms of the element occupy *all* the positions. This arrangement is of particular interest in that it places each atom equidistant from four others. The closeness of the packing suggests that the atoms are held by primary valence bonds.

Type F is the "calcium fluoride" arrangement. It is one of the arrangements in which salts which contain two atoms of one kind and one of another crystallize. Examples are calcium, strontium and barium fluorides. In this arrangement, the atoms, of which kind there is only one in the molecule, let us say those of calcium in calcium fluoride, are arranged on a face-centered lattice. The atoms of the other kind, fluorine in this example, are arranged on two other face-centered lattices which penetrate the first so as to bring a fluorine atom at the center of each of the eight small cubes of the face-centered cube.

Type G is the "cuprous oxide" arrangement. This is the alternative cubic arrangement for compounds of the type AB_2 or A_2B and is the structure of cuprous and silver oxides. The simplest way of regarding the arrangement is to think of it as consisting of a body-centered lattice of the atoms of which there is only one in the molecule (oxygen, in the case of cuprous oxide, Cu_2O), penetrated by a face-centered lattice on which lie *all* the atoms of the other kind (copper in the case of cuprous oxide), bringing the latter atoms at the centers of the alternate small cubes into which the body-centered lattice is divisible.

Two other types of arrangements more or less frequently met with belong to the hexagonal system. These are the "hexagonal close-packed" and the "zinc oxide" arrangements.

The hexagonal close-packed arrangement is shown in Fig. 7. It represents the arrangement of atoms in many metals. The fundamental cell in this type is a prism with an equilateral triangle as its base. There is an atom at each of the six corners of this prism. Six of these prisms may be fitted together to give a hexagonal prism (shown in the figure). Three more atoms are now to be placed at the centers of alternate triangular prisms. These form part of a second lattice interpenetrating the first. When the ratio of the side to the altitude of the prism is as 1 : 1.633, the distance from one corner to the center of the prism is equal to the side-length. Under these circumstances each atom is equidistant from 12 others.

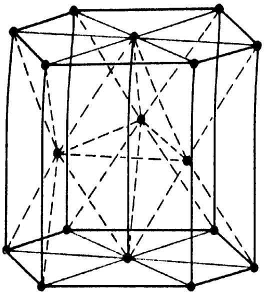

FIG. 7. Hexagonal Close-packed Lattice

In the "zinc-oxide" arrangement two hexagonal close-packed arrangements, one carrying the zinc atoms and the other the oxygen atoms, interpenetrate. The resulting arrangement is difficult to visualize or to draw. The essential point is that it brings the atoms of one kind into positions such that they are equidistant from four of the other kind. Consider one of those prisms of the hexagonal close-packed arrangements which contains an atom at its center. If the ratio of side to altitude is as 1 : 1.633, the atom at the center and the three atoms at the corners of the base are at the corners of a regular tetrahedron. In the "zinc oxide" arrangement an atom of the other kind will lie at the center of this tetrahedron. The "zinc oxide" arrangement, therefore, bears the same relation to the hexagonal close-packed arrangement as does the "diamond" to the face-centered cubic arrangement.

One other type of structure is of special interest in connection with the subject of isomorphism. This is the "calcite" arrangement. The crystallographic axes are of equal lengths and inclined to one another at equal angles other than 90°. The unit cell may be regarded as a distorted cube. In calcite the calcium and carbon atoms are arranged in the same fashion as are the sodium and chlorine atoms in the "sodium chloride" arrangement, that is, the "calcite" arrangement might be characterized as distorted simple cubic. The oxygen atoms are arranged in sets of three around the carbon atoms and close to the latter, showing that the carbonate ion maintains its identity in the crystalline state. The minerals dolomite ($CaMg(CO_3)_2$), rhodocrosite ($MnCO_3$), and siderite ($FeCO_3$) and the compound $NaNO_3$ all have the calcite arrangement.

In the following table are given the type of arrangement, the length of side of the unit cell and the distance apart of nearest atomic centers in crystals of a number of substances. The types of arrangements are abbreviated as follows: face-centered cubic (F.C.C.), body-centered cubic (B.C.C.), simple, cubic or "sodium chloride" (NaCl), "cæsium chloride" (CsCl), "diamond" (Diam.), "zinc sulphide" (ZnS), "calcium fluoride" (CaF_2), "cuprous oxide" (Cu_2O), hexagonal close-packed (H.C.P.), "zinc oxide" (ZnO). For the dimensions of the unit cell, the length of side is given for cubic crystals and the side of the triangular prism and ratio of altitude to side for hexagonal crystals. The distance apart of atomic centers refers to the distance between nearest centers of like atoms in elements and of unlike atoms in compounds. Distances are given in Ångstrom units (1 Å. = 10^{-8} cm.).

TABLE I

Crystal Structure and Interatomic Distances

Elements				Compounds			
Substance	Type	Side of Unit Cell, Å.	Distance between Nearest Centers, Å	Substance	Type	Side of Unit Cell, Å.	Distance between Nearest Centers, Å.
Al	F.C.C.	4.07	2.88	BeO	ZnO	2.70	1.65
Ca	"	5.56	3.93			(1.63)	
Ni	"	3.54	2.51	MgO	NaCl	4.20	2.10
Co	"	3.55	2.51	CaO	"	4.76	2.38
Cu	"	3.61	2.55	SrO	"	5.10	2.55
Rh	"	3.82	2.70	BaO	"	5.48	2.74
Pd	"	3.95	2.80	NiO	"	4.15	2.08
Ag	"	4.06	2.87	CdO	"	4.72	2.36
Ir	"	3.81	2.69	ZnO	ZnO	3.22	1.97
Pt	"	3.93	2.78			(1.60)	
Au	"	4.07	2.88	MgS	NaCl	5.08	2.54
Ce	"	5.12	3.62	CaS	"	5.64	2.82
Pb	"	4.91	3.47	SrS	"	5.87	2.93
Th	"	5.10	3.56	BaS	"	6.40	3.20
Li	B.C.C.	3.50	3.03	MnS	"	5.21	2.61
Na	"	4.30	3.72	PbS	"	5.80	2.90
K	"	5.20	4.50	ZnS	ZnS	5.42	2.35
V	"	3.04	2.63	CdS	ZnO	4.16	2.54
Cr	"	2.90	2.51			(1.62)	
Fe	"	2.86	2.47	SnS	"	3.60	
Mo	"	3.14	2.72			(2.20)	
W	"	3.15	2.73	SrSe	NaCl	6.20	3.10
Mg	H.C.P.	3.22	3.22	ZnSe	ZnS	5.65	2.45
		(1.62)		LiCl	NaCl	5.17	2.59
Ti	"	2.97	2.97	LiBr	"	5.48	2.74
		(1.59)		LiI	"	6.06	3.03
Co	"	2.51	2.51	NaF	"	4.65	2.33
		(1.63)		NaCl	"	5.63	2.91
Zn	"	2.67	- -	NaBr	"	5.95	2.98
		(1.86)		NaI	"	6.47	3.24
Zr	"	3.23	3.23	KF	"	5.36	2.68
		(1.59)		KCl	"	6.26	3.13
Ru	"	2.69	2.69	KBr	"	6.59	3.30
		(1.59)		KI	"	7.11	3.56
Cd	"	2.96	-	RbCl	"	6.60	3.30
		(1.89)		RbBr	"	6.93	3.47
Ce	"	3.65	3.65	RbI	"	7.36	3.68
		(1.62)		CsCl	CsCl	4.12	3.56
Os	"	2.71	2.71	CsBr	"	4.30	3.72
		(1.59)		CsI	"	4.55	3.94

TABLE I—*Continued*

Elements				Compounds			
Substance	Type	Side of Unit Cell, Å.	Distance between Nearest Centers, Å.	Substance	Type	Side of Unit Cell, Å.	Distance between Nearest Centers, Å.
C (diamond) .	Diam.	3.55	1.54	TlCl .	CsCl	3.85	3.33
				AgCl . . .	NaCl	5.54	2.77
Si . .	"	5.43	2.35	AgBr	"	5.77	2.88
Ge . . .	"	5.62	2.44	AgI . .	ZnS	6.49	2.81
Sn (grey)	"	6.46	2.80	AgI .	ZnO	4.59 (1.633)	2.81
				CuCl .	ZnS	5.49	2.38
				CuBr .	"	5.82	2.52
				CuI . .	"	6.10	2.63
				CaF_2	CaF_2	5.49	2.38
				SrF_2	"	5.77	2.50
				BaF_2 .	"	6.20	2.69
				Cu_2Se	"	5.75	2.49
				Cu_2O . . .	Cu_2O	4.30	1.86
				Ag_2O	"	4.73	2.05

The Structure of Crystals from the Chemical Standpoint. *Salts:* One of the most interesting facts which has developed from X-ray analysis of crystal structure is that in crystals of salts (including oxides and sulphides), the chemical molecule, as it is ordinarily thought of and as it would conceivably exist in the vapor phase, has completely lost its identity. Thus, in a crystal of potassium chloride, each potassium atom has equidistant from it six chlorine atoms, each of which in its turn is equidistant from six potassium atoms. No pair of potassium or chlorine atoms can be singled out and said to constitute a chemical molecule, since each atom belongs as much to five other atoms of the other kind as it does to the one with which it is arbitrarily paired.

Similar considerations apply to salts of oxygen acids so far as the disappearance of the molecule is concerned, but the association of the atoms of the acid radical apparently carries over into the crystal. Thus, in calcite, three oxygen atoms are grouped around each carbon atom, the distance between C and O centers being 1.28 Å. whereas the distance between the centers of the nearest Ca and O atoms is 2.42 Å.

Diamond and Graphite: With respect to the non-existence of any molecule in the ordinary sense, a crystal of diamond is similar to those of salts. Each carbon atom is surrounded by four others which are equidistant from it and each of these is in its turn surrounded by four. The structure may in fact be thought of as the ultimate in the branching of carbon chains, the crystal itself being a sort of giant molecule. The attachment of each carbon atom in diamond to four others of course recalls at once the quadrivalence of carbon in organic compounds. Another structural feature of carbon compounds which is discernible in the diamond lattice is the six-membered ring. This ring is made up of the atoms at the centers of three adjacent faces of the face-centered lattice and of three of the four atoms which lie at the centers of the small cubes. The atoms are not all in one plane but the para atoms are one below and one above the plane of the other four. The rings are not isolated but are built out, as are those in naphthalene and anthracene, except that they are extended in two dimensions instead of one. Thus, each carbon atom occupies the ortho position in two rings and the para position in one. The rings occur in planes perpendicular to the body diagonal of the cubic lattice.

In graphite, the branched-chain structure of diamond is lost, but the ring structure remains. In diamond, the nearest atoms in two adjacent planes which contain the rings are 1.54 Å. apart, which is also the distance apart of adjacent atoms in the ring. In graphite, these planes have been separated till the nearest atoms in adjacent planes are 3.25 Å. apart (over twice as great a spacing as in diamond) and adjacent atoms in the ring have been drawn slightly together, their distance apart being 1.50 Å. The planes are not oriented to one another in quite the same way in the two structures. The relation between the two is shown in Fig. 8.

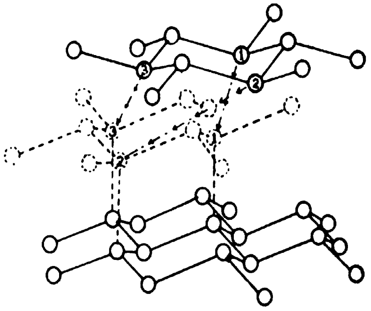

Fig. 8 Diamond-Graphite Relationship

The wide spacing of the planes in graphite leaves each atom closely attached to only three others. This fact, with the existence of the rings, suggests the planes in graphite as giant molecules of the aromatic series of the type of naphthalene and anthracene, the rings being extended in two dimensions. The weakness of the binding between adjacent planes is emphasized by the fact that the familiar cleavage of graphite occurs along these planes.

Organic Compounds: The X-ray analysis of crystals of organic compounds offers considerable difficulty because of their low symmetry and the unquestionable complexity of the arrangements. Some interesting beginnings have been made, however. Thus, Sir W. H. Bragg[1] has deduced probable structures for naphthalene, anthracene and some related substances. These are in agreement with the assumption that the six-membered ring as it exists in diamond and graphite is also present in these substances, as has been assumed in organic chemistry. The integrity of the molecule is thus in all probability maintained, contrary to the case in crystals of salts. Indeed, it is difficult to believe that it could have been otherwise when the almost infinite possibilities of rearrangement are taken into account. The fact that optically active substances are not racemized on crystallization, when so slight a change would accomplish this result if the arrangement were once broken up, is enough to establish this.

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[1] *Proc. Phys. Soc. London*, **34**, 33 (1921).

The structure of tartaric acid has also been recently investigated in Bragg's laboratory by Astbury.[1] Although the X-ray method is not capable of distinguishing between the enantiomorphous (mirror image) forms, the existence of a spiral arrangement was established.

Isomorphism: Many groups of substances which are similar in chemical constitution exhibit almost complete identity of crystalline form. Such substances are said to be isomorphous. Mitscherlich, who first observed the fact in connection with the rhombic forms of $Na_2HPO_4.12H_2O$ and $Na_2HAsO_4.12H_2O$, and who proposed the term isomorphism, believed that the identity of form was complete and assumed that the substances contain the same number of atoms arranged in the same fashion. Recent measurements by Tutton[2] on the rhombic sulphates and selenates and monoclinic double sulphates and selenates of the alkali metals have shown conclusively that the crystals of the members of these isomorphous series are not exactly alike but differ slightly in the values of the axial ratios, the variation in the latter and in various physical properties revealing a regular progression in passing from one member of the series to the next. This is illustrated by the following values of the axial ratios of the first series of substances. While the differences are slight, they are nevertheless real.

TABLE II

THE AXIAL RATIOS OF THE ISOMORPHOUS SERIES $R_2\left(\begin{matrix}S\\Se\end{matrix}\right)O_4$

(R = alkali metal. The crystals are orthorhombic)

Salt	Axial Ratios		
	a	: b :	c
K_2SO_4	0.5727	: 1 :	0.7418
Rb_2SO_4	0.5723	: 1 :	0.7485
Cs_2SO_4	0.5712	: 1 :	0.7531
K_2SeO_4	0.5731	: 1 :	0.7319
Rb_2SeO_4	0.5708	: 1 :	0.7386
Cs_2SeO_4	0.5700	: 1 :	0.7424

It is in general characteristic of isomorphous substances that when a solution containing two such substances is evaporated, the two will crystallize out together forming mix-crystals, which are single crystals containing both substances. Further, when a crystal of one such substance is placed in a super-saturated solution of another, the second substance will crystallize out or overgrow on the first just as it would on a crystal of itself. Molecules of such substances are therefore capable of fitting into or onto the crystal lattices of one another. These properties had acquired great importance as tests for isomorphism prior to the discovery of the X-ray method of analysis of crystal structure and had indeed been adopted by many writers as the essential prerequisites of isomorphous substances. This view has introduced many difficulties, however, and has tended to complicate the whole subject. For example, sodium and potassium chlorides crystallize in the same forms and it is now known that they have the same crystal structures, yet they do not form mix-crystals. On the other hand, mix-crystals of potassium and ammonium chlorides, and of potassium and ammonium salts generally, may be obtained, although the crystals of these substances are not alike, though both are cubic, and the numbers of atoms in the molecule (though not the number of potential ions, of course) are different. It is probable that, in order that two substances shall form mix-crystals, it is necessary that the volume and general form of the structural units shall not be very different. Other agencies are undoubtedly at work, however, since mix-crystals of substances as different as ammonium chloride and ferric chloride can be obtained.

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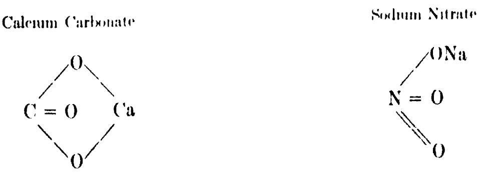
[1] *Proc. Roy. Soc.*, December, 1922.

[2] Tutton, Crystalline Structure and Chemical Constitution (MacMillan, 1910).

Another difficulty in the way of the use of mix-crystal formation as a criterion of isomorphism is that one of the substances considered may have a very low solubility. This difficulty is introduced in the case of sodium nitrate and calcium carbonate (in the form of calcite). These substances both crystallize in the trigonal system, forming rhombohedra whose axes are inclined to one another at almost the same angles, namely, 106° 33′ for sodium nitrate and 105° 5′ for calcium carbonate, and X-ray examination has shown that the two have exactly the same crystal structures (see above). The two substances are, therefore, isomorphous. In addition, their molecular volumes are not very different (in cc. per gm. mol., 37.5 for $NaNO_3$ and 36.9 for $CaCO_3$). Since, however, calcium carbonate is practically insoluble, mix-crystals cannot be obtained, though sodium nitrate can be made to overgrow on calcite.

Because mix-crystals of sodium nitrate and calcium carbonate could not be obtained, even though this was for the practical reason that calcium carbonate is insoluble, it has been denied that the two are in fact isomorphous. The disinclination to regard them as isomorphous resulted from the fact that their structures were different on the old method of writing formulæ. Langmuir[1] has cleared up this and many other disputed cases of isomorphism by showing that on the basis of the Lewis theory of valence, the two have in fact the same structures which are as given below.

OLD STRUCTURES


Calcium Carbonate

Sodium Nitrate

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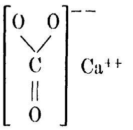
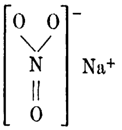
[1] Langmuir, *J. Am. Chem. Soc.*, **41**, 1543 (1919).

NEW STRUCTURES

(A pair of shared electrons is represented by one bond.)





The only difference between the two is that in the first the ions are doubly charged and in the second they are singly charged.

Polymorphism: It often happens that a substance can occur in more than one crystalline form. When this is the case, the substance is said to be polymorphic. The different polymorphic modifications ordinarily belong to different crystal systems, though there are exceptions. A familiar example is sulphur, which has a rhombic modification, stable up to 95.6°, and a monoclinic modification, stable between 95.6° and 119.25° (its melting point).

Polymorphism results from different space-lattice arrangements of the same chemical units, as is attested by the fact that the modifications usually belong to different crystal systems. The crystal structures have only been worked out in a few cases. Thus, carbon occurs as diamond and as graphite, the structures of which have already been discussed. Silver iodide occurs in a hexagonal and in a cubic form. In the first, it has the ZnO structure and in the second, the ZnS structure. Ammonium chloride is an example of a substance having two modifications which both crystallize in the same system (the cubic). The high temperature modification has the sodium chloride structure and the low temperature modification has the cæsium chloride structure.

Polymorphic modifications may or may not be interconvertible. When they are interconvertible (e.g., $S_{rh} \overset{96\ 5^\circ}{\rightleftharpoons} S_{monocl}$), the change is said to be enantiotropic. When the change can only take place in one direction, that is, when one form is metastable under all conditions investigated, it is said to be monotropic, as Diamond → Graphite or Aragonite → Calcite. Since such forms as diamond and aragonite have remained as such through geologic ages, it is evident that the conversion of polymorphic modifications may be exceedingly slow. This is to be compared to the rapidity with which equilibrium is reached in the transition of solid to liquid. Further discussion of solid-solid transitions will be found in Chapter IX, "Heterogeneous Equilibrium."

SOLID-LIQUID TRANSITION

The melting point of a pure crystalline solid may be defined as the temperature at which it is in equilibrium with the corresponding pure liquid. This temperature depends upon the pressure on the system, the variation being given by the Clapeyron equation.

It is probably safe to say that, as a general rule, a crystalline solid undergoes spontaneous transformation into the liquid phase when the melting point is reached; that is, a crystalline solid cannot be superheated. Nevertheless, it must be stated that, as experimentally determined, melting points sometimes appear not to be sharp. This was found to be the case for the silicate minerals, diopside, anorthite, and the like, by Day and Sosman,[1] and for betol and dextrose by Tammann.[2] These investigators found that, while melting always set in at a definite temperature, it was possible to heat the solid several degrees above this point during the process of melting. These results seem to show that melting takes place with independent finite velocity even above the melting point rather than that the rate is dependent solely upon the rate of supply of heat at the melting point.

The freezing point of a liquid is identical with the melting point of the corresponding solid when the latter is defined as the temperature at which pure solid and liquid are in equilibrium at a given pressure. The freezing point of a liquid does not mark off the limit of existence of the liquid phase, however, for if a liquid is carefully freed from suspended solid, especially particles of the corresponding solid phase, and is protected from vibrations and sudden changes, it may often be cooled many degrees below the freezing point. Under these conditions the velocity of crystallization may be negligibly small. It is to this possibility that glasses owe their existence. An extended study of the velocity of crystallization of supercooled liquids has been carried out by Tammann.[3] This investigator found that two factors have to be taken into account: (1) the rate of formation of crystal nuclei and (2) the rate of growth of the latter below the melting point. Both rates pass through maxima with diminishing temperature but the maxima occur at different points. With piperin, whose melting point is 129° C., the rate of formation of crystal nuclei was greatest at 40° C. and practically negligible above 80° and below 0° C. The rate of growth of the nuclei was a maximum at 100° and negligibly small at the melting point. Similar results were obtained for betol and a number of other substances. With many substances, however, the temperatures for the maximum rates of nucleus formation and nucleus growth lie so close to one another and to the melting point that measurements are difficult. For such substances practically no supercooling is possible.

Each polymorphic modification of a substance has its own particular melting point. For example, rhombic sulphur melts at 113° while monoclinic sulphur melts at 119.25°. Consequently, in giving a melting point, the polymorphic modification to which it refers should also be stated. Of two polymorphic modifications, that which is metastable in the melting point region has the lower melting point.

For further information on solid-liquid transitions, Chapter IX on Heterogeneous Equilibrium should be consulted.

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[1] *Z. anorg. Chem.*, **72**, 1 (1921).

[2] *Z. physik. Chem.*, **68**, 252 (1910).

[3] See Tammann, Kristallisieren und Schmelzen, Leipzig, 1903, J. A. Barth. See also Chapter XV.

THE COMPRESSIBILITY AND THERMAL EXPANSION OF CRYSTALLINE SOLIDS

The P, V, T relations of crystalline solids are complex and, as yet, the kinetic-molecular theory of the solid state is only in the preliminary stages of development. Part of this complexity arises from the fact that, except in the cubic system, the properties of crystals vary when measured in different directions through the crystal, that is, crystals are anisotropic. Thus, when a crystal of silver iodide is heated, it contracts in one direction while expanding in another.

It is generally assumed that the units of the crystal lattice (atoms or molecules) are confined as to motion to vibrations about equilibrium positions in the lattice. This equilibrium results from the action of attractive and repulsive forces between the constituents of the lattice. There has recently been much speculation as to the nature of these forces and of the characteristics of the motions of atoms in the lattice, references to which will be found in the sections on thermodynamics and quantum theory.

Numerous measurements of the P, V and V, T relations of solids have been made. These are usually stated in terms of the coefficients of compressibility and thermal expansion. The volume coefficients are

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \text{and} \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P .$$

These express the fractional change in volume per unit increase of pressure and of temperature. Sometimes the linear coefficients are given instead of the above. These refer to the fractional changes in length. For cubic crystals, whose properties are the same in three directions—and which are therefore isotropic—the linear coefficients are very nearly equal to 1/3 of the volume-coefficients.

The coefficients of expansion and compressibility are very small. Thus, the coefficients of compressibility for the solid elements vary from 61×10^{-6} for cæsium down to 0.16×10^{-6} for diamond. These are for pressures expressed in megabars[1] (10^6 dynes per sq. cm.). Values of the coefficients of compressibility and of expansion at 20° C. for a number of substances are given in Table III. There have also been added to the table the melting points, molecular volumes and crystal data.

It may be assumed that the atoms of a solid hold their normal distances apart as the result of a balance of attractive and repulsive forces. The attractive force gives rise to the cohesion of the solid. It is clear that thermal expansion must take place against this force and will therefore be small when the cohesive force is large. Compression, on the other hand, must take place against the repulsive forces. Since, however, the two are normally balanced against one another, the repulsive force must be large and therefore the compressibility small, when the cohesive force is large. These two properties should therefore vary from one solid to another in the same way and this is

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[1] The megabar is 1.33 per cent less than the atmosphere.

TABLE III

Physical Properties of Solids

β = coefficient of compressibility × 10^6, for pressure measured in megabars.
α = coefficient of thermal expansion, × 10^5.
M.P. = melting point in degrees, absolute.
V = atomic or molecular volume in cc.
d = distance between nearest atoms in the crystal lattice, in Ångstroms (= 10^{-8} cm.).

Substance	β	α	M.P.	V	Space-lattice	d
Li	9.0	19.0	453	13.1	B.C.C.	3.03
B	0.3	—	2800	4.7	—	—
C (diamond)	0.16	0.3	Very high	3.4	Diam.	1.54
C (graphite)	3.0	7.2	Very high	5.4	—	1.50
Na	15.6	22.0	371	23.7	B.C.C.	3.72
Mg	2.9	7.8	927	13.3	H.C.P.	3.22
Al	1.47	7.2	930	10.1	F.C.C.	2.88
Si	0.32	2.3	1733	11.4	Diam.	2.34
P (red)	0.52	—	863	14.6	—	
P (white)	20.5	36.0	317	16.6	—	—
S	12.9	18.0	384	15.5		—
K	31.7	25.0	335	45.5	B.C.C.	4.50
Ca	5.7	—	1073	25.3	F.C.C.	3.93
Cr	0.9	—	1823	7.7	B.C.C.	2.51
Mn	0.84	—	1533	7.7	—	—
Fe	0.60	3.6	1790	7.1	B.C.C.	2.47
Ni	0.43	4.2	1725	6.7	F.C.C.	2.51
Cu	0.75	5.0	1356	7.1	F.C.C.	2.55
Zn	1.7	8.7(?)	692	9.5	H.C.P.	2.67
As	4.5	1.6	1073	13.3	—	—
Se	12.0	13.0	490	18.5	—	—
Rb	40.0	30(?)	312	56.0	—	—
Mo	0.46	1.1	2773	11.1	B.C.C.	2.72
Pd	0.54	3.8	1822	9.3	F.C.C.	2.80
Ag	1.01	5.7	1234	10.3	F.C.C.	2.87
Cd	2.1	7.4	594	13.0	H.C.P.	2.96
Sn	1.9	6.7	505	16.2	—	—
Sb	2.4	3.3	903	17.9	—	—
I	13.0	25.0	386	25.7	—	—
Cs	61.0	33(?)	301	71.0	—	—
Ta	0.53	2.3	3123	10.9	B.C.C.	2.83
W	0.27	1.1	3300	0.6	B.C.C.	2.73
Pt	0.38	2.7	2020	9.1	F.C.C.	2.78
Au	0.64	4.3	1336	10.2	F.C.C.	2.88
Tl	2.3	9.0	574	17.2	—	—
Pb	2.32	8.8	600	18.2	F.C.C.	3.47
Bi	3.0	4.0	543	21.2	—	—
NaCl	4.27	12.1	1077	27.1	NaCl	2.81
NaBr	5.24	—	1031	32.1	NaCl	2.98
NaI	7.05	—	926	40.8	NaCl	3.24
KCl	5.19	—	1045	37.6	NaCl	3.13
KBr	6.39	12.6	1003	43.4	NaCl	3.30

TABLE III—*Continued*

Substance	β	α	M.P.	V	Space-lattice	d
KI	8.75	12.9	953	53.1	NaCl	3.56
AgCl	2.38	13.2	724	25.8	NaCl	2.78
AgBr	2.75	10.5	700	29.0	NaCl	2.89
AgI	4.09	—	—	41.4	ZnS	2.81
TlCl	4.1	—	699	34.1	CsCl	3.34
TlBr	5.3	—	723	37.6	—	—
TlI	6.98	—	704	46.7	—	—
CaF_2	1.2	5.7	1575	24.7	CaF_2	2.35
MgO	0.70	2.8	3000	11.0	NaCl	2.10
PbS	1.95	6.0	1288	31.2	NaCl	—

found to be the case. Thus, among the solid elements, the alkali metals are found to have the greatest compressibilities and also the greatest expansion coefficients and correspond therefore to minima in the cohesive forces. Two other properties, atomic (or molecular) volume and melting points, in all probability also bear a relation to the cohesive forces. A large cohesive force should result in a relatively small atomic volume and a high melting point. The small atomic volume obviously corresponds to a large attraction between the atoms. The melting point represents the limit to which a solid can be heated and maintain its form. Rise in temperature corresponds to the input of energy, some of which, as kinetic energy, works against the cohesive forces. If these forces are small, a relatively small input of energy and therefore a relatively low temperature is sufficient to overcome them and bring about destruction of the lattice and hence melting.

HEAT CAPACITIES OF CRYSTALLINE SOLIDS

The Law of Dulong and Petit: The atomic heat capacities of a large number of crystalline solids when measured in the vicinity of room temperature approximate to the value 6 calories per degree. In so far as this applies to the elements, it is known as the law of Dulong and Petit. This is true of the metallic elements and of a number of halides and sulphides, as may be seen in the following table. The "atomic" heat capacities of compounds are calculated by dividing the product of specific heat and molecular weight by the number of atoms in the molecule. At the end of the table are given values for the atomic heat capacities of some of the lighter solid non-metallic elements and of solid compounds containing such elements as oxygen and carbon. It will be seen that these deviate markedly from the rule.

The above values are those determined at constant pressure. Lewis has shown that the values of the atomic heat capacity at constant volume, calculated from the above by the thermodynamic relation

$$C_v = C_p - 0.02423 \frac{\alpha^2 VT}{\beta}$$

TABLE IV

ATOMIC HEAT CAPACITIES AT ROOM TEMPERATURE

Elements		Compounds	
	Atomic Heat Capacity		Atomic Heat Capacity
Li	6.6	NaCl	6.4
Na	6.9	KCl	6.2
Mg	6.0	KI	6.8
Al	5.8	AgCl	6.5
K	7.1	AgI	6.7
Ca	6.0	TeCl	6.3
Fe	6.0	PbS	5.9
Cu	5.8	$PbCl_2$	6.2
Zn	6.0	Sb_2S_3	5.7
Ag	6.1		
Pt	6.1	SiC	3.2
Te	6.4	MgO	4.8
Pb	6.3	CuO	5.2
		Al_2O_3	4.1
B	2.8	Fe_3O_4	5.1
C (diamond)	1.6	$CaCO_3$	4.1
C (graphite)	2.0	$H_2C_2O_4$	3.1
Si	4.5		
I	6.9		

in which

V = Atomic volume,
β = Compressibility,
α = Expansion coefficient,

are in somewhat closer agreement than the constant pressure values. There still remain marked deviations, however.

One reason for the partial failure of the law of Dulong and Petit lies in the arbitrary choice of room temperature as the temperature of comparison. Investigation of the change of heat capacity with temperature has revealed that this law is subordinated to a more general one which states that atomic heat capacity at constant volume increases with the temperature to a maximum value which is in the neighborhood of 6 calories per degree for all substances.[1] This constant maximum has already been reached at room temperature by those substances which obey the law of Dulong and Petit, and their heat capacities are nearly independent of the temperature at room temperature. The heat capacities of those other substances which deviate from the law are still increasing more or less rapidly with the temperature and presumably will reach a maximum at much higher temperatures. Thus, for example, the atomic heat capacity of diamond has risen to 5.45 calories per degree at 1169° K., from the value of 1.6 calories per degree at room temperature.

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[1] See, however, Eastman, Williams and Young, *J. Am. Chem. Soc.*, **46**, 1178, 1184 (1924).

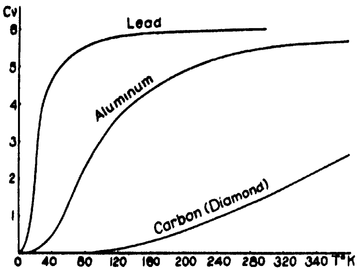

FIG. 9. Atomic Heats of Lead Aluminum and Diamond

Heat Capacity and Temperature: In Fig. 9 are plotted values of atomic heat capacity against temperature for three typical substances. It will be seen that for two of these the heat capacity approaches a value in the neighborhood of 6 at the higher temperatures. As the temperature is lowered, a region is encountered in which the heat capacity falls off rapidly and, in the case of at least one substance (diamond) and probably of many, becomes immeasurably small at temperatures considerably above the absolute zero.

It is apparent that the heat capacity-temperature curves are of the same character. Lewis and Gibson[1] have demonstrated that the atomic heat capacities at constant volume are expressible as functions of the temperature for a large number of substances by the equation

$$C_v = F\left(\frac{T}{\theta}\right)^n,$$

in which F is the same function for all,[2] and θ and n are constants characteristic of the particular substance. The constant, θ, has the dimensions of temperature and may be set equal to the temperature at which $C_v = \frac{3}{2}R = 2.98$ cals. Substances may be divided into two classes with respect to the value of n. For the elements which crystallize in the cubic system, and for thallium, zinc and solid mercury and for the alkali halides as far as investigated, n is equal to unity (Class I). For other substances n has values less than unity,

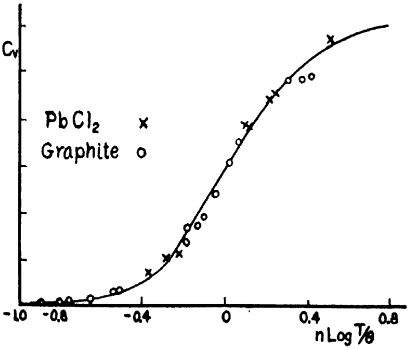

FIG. 10. C_v—$n \log T/\theta$ for Graphite and Lead Chloride

ranging from 0.90 for thallous chloride down to 0.31 for solid benzene (Class II).

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[1] *J. Am. Chem. Soc.*, 39, 2554 (1917).

[2] A discussion of the probable form of this function will be found in Chapter XVII.

If the above relation is correct, plots of the value of C_v against $n \log \frac{T}{\theta}$ for different substances should lie on the same curve. Such values have been plotted in Fig. 10 for graphite and lead chloride of Class II. The values of n and θ for different substances which give the same curve as in Fig. 10 are recorded in the following table.

TABLE V

VALUE OF n AND θ

	n	θ	$\log \theta$
Lead	1	22.0	1.342
Diamond	1	461	2.664
Potassium chloride	1	56	1.75
Graphite	0.789	393	2.594
Lead chloride	0.796	45.7	1.660

THE MESOMORPHIC STATE (LIQUID CRYSTALS)

The majority of substances may be obtained in one or more crystalline phases, a liquid phase and a vapor phase only. It appears, however, that a restricted group of organic substances are capable of forming yet another phase intermediate both as to occurrence and as to properties between the crystalline and liquid phases. Substances in this state have been termed "liquid crystals" to indicate their transitional character

It should be understood that liquid crystals do not combine the properties of the liquid and crystalline states. If our ideas as to the ultimate natures of these states are correct, this would be an obvious impossibility, since in the one state the constituent particles are assumed to be distributed at random and in the other state to be arranged in definite space-patterns of greater or less symmetry, all obeying the one fundamental law of rational indices. The particles obviously cannot be at the same time both in a random arrangement and in a definite geometrical arrangement obeying the law of rational indices. Rather, the properties of liquid crystals indicate that these are intermediate between the two states in the sense that while there may be a primitive arrangement of molecules in one plane or around a common axis, this arrangement is not sufficiently elaborate to permit obedience to the law of rational indices. Since the term "liquid crystals" may lead to misunderstanding of the true nature of substances in this state and since it seemingly subordinates the state to the liquid and the crystalline, whereas it actually possesses its own peculiar characteristics, it has been suggested that this designation be abandoned and the term "mesomorphic state" substituted.[1]

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[1] G. Friedel, Annales de Physique [9], **18**, 272-474 (1922). This 200-page paper contains the most recent account of the properties (especially the optical properties) of liquid crystals.

As an example of a substance yielding a mesomorphic phase, we may take cholesteryl benzoate, the first of such substances to be discovered. Cholesteryl benzoate, which is a crystalline solid at room temperature, melts sharply at 145.5° to a cloudy, viscous liquid, the mesomorphic phase. This is stable up to 178.5°, at which temperature it undergoes an abrupt transition to a clear mobile liquid. The most striking property of the mesomorphic phase is its bi-refringence. Bi-refringence or double refraction consists in the ability to resolve a beam of incident light into two polarized, refracted beams. When a bi-refringent substance is examined between nicol prisms set at right angles, the normally dark field is lightened. That this is not due to optical activity of the ordinary kind is shown by the fact that there is no position of the analyzing prism at which the field becomes dark again, whereas if the prisms are kept at right angles and rotated together, extinction does occur.

Prior to the discovery of liquid crystals, bi-refringence had been observed in the majority of crystals (all except those of the cubic system) in liquids placed in a strong electrostatic or magnetic field, and in amorphous solids subjected to a mechanical stress. The bi-refringence, moreover, had been successfully ascribed to a lack of symmetry within the substance such that physical properties had different numerical values according as they were measured in one or another direction through it. Such substances are said to be anisotropic. Gases, ordinary liquids and crystals of the cubic system are isotropic, the first two being so because of their complete lack of symmetry and the latter because of their very high symmetry. Mesomorphic substances are obviously not crystalline in the ordinary sense, nor are they under any externally applied stress. To account for their bi-refringence and therefore their anisotropic character, it seems necessary to assume that the molecules of such substances are not distributed at random as in an ordinary fluid but in some regular manner, however primitive the arrangement may be when compared to the arrangement of atoms in crystals.

This assumption of molecular orientation is further borne out by the interesting forms which liquid crystals assume. Perhaps the most extraordinary of these are the so-called graded drops (*les gouttes à gradins*). When a small mass of ethyl para-azoxybenzoate, for example, is fused on a carefully cleaned glass plate or a freshly-cut cleavage surface of mica, it does not wet the surface but draws up into a drop whose upper surface is smooth and perfectly plane and whose edges are graded off into steps. The drop appears to be built up of a pile of planes which, when the drop is touched, glide over one another easily and recall the cleavage planes of crystals. It appears probable that these planes are of molecular dimensions in thickness (about 50 Å.). Their edges are made visible under the microscope by the fact that they are terminated by chains of very fine droplets which are bi-refringent.

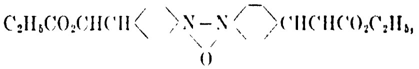
Other structures, some of them strongly resembling crystalline forms with edges rounded off, are met with when certain of these substances separate from solution. Ammonium oleate yields such forms, resembling double cones, when it separates from an alcoholic solution. When either ethyl para-azoxybenzoate or ammonium oleate is melted on glass so that it wets the surface, it may show a fan-like structure or that of a colony of particles of elliptical or spherical cross section.

In another group of mesomorphic substances, of which para-azoxyphenetol is an example, filiform (thread) structure is visible. The threads are variable in number, appearing in especially large quantity when the preparation is placed in an electro-static field, in which they orient themselves along the lines of force.

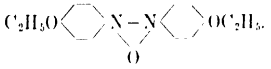
In all the above examples, evidence of a tendency to molecular orientation, producing a structure of some sort, is apparent. It might therefore be expected that the substances would have some effect on X-rays, such as crystals do. Attempts to obtain diffraction effects of this nature have so far been unsuccessful; but it should be pointed out that the forms which would seem to be most suitable to the test, namely, the graded drops, have not as yet been tried. According to the best opinion, the molecules of substances in the mesomorphic state occur in groups having a common axis

About 250 substances which yield a mesomorphic phase have been prepared up to the present. All are organic compounds having a long straight-chain which may contain para-substituted rings. Examples of the various types are:

Ammonium oleate $C_{17}H_{33}COONH_4$,

Ethyl para-azoxybenzoate 

Cholesteryl acetate $CH_3COO.C_{26}H_{43}$,

Para-azoxyphenetol 

For further information on the subject of liquid crystals, the reader is referred to Friedel's paper mentioned above and to "Flussige Krystalle" by Lehmann (Engelmann, Leipzig, 1904) and "Kristallinische Flussigkeiten und Flussige Kristalle" by Schenck (Engelmann, Leipzig, 1905).

CHAPTER VI

THERMOCHEMISTRY

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The heat effects accompanying such familiar reactions as the combustion of fuel early attracted much attention. Boyle, Lavoisier, Laplace, Dulong, Davy and Rumford all concerned themselves with thermochemical investigations but their experiments were of too rough a nature to be of much value quantitatively. The beginnings of modern thermochemistry were practically contemporaneous with the doctrine of the conservation of energy. Thermochemistry treats of the *heat effects* and *internal energy changes* accompanying chemical reactions. We speak of endothermic and exothermic reactions, meaning those that take place with an absorption or evolution of heat.

Quantities of heat are usually expressed in terms of the heat capacity of water for a 1° temperature change. It is only of late years from the work of Rowlands,[1] Griffiths [2] and Callendar and Barnes [3] that it has been realized that the specific heat of water varied with the temperature. Hence, the calorie is only fully defined when the particular degree of temperature is specified through which unit mass of water is heated.

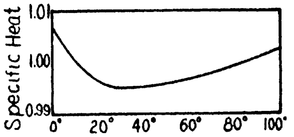

Fig. 1 Specific Heat of Water

Two units have been used to measure amounts of heat, the 15° calorie which is equal to the amount of energy required to raise the temperature of one gram of water from 15° to 16° C. and the mean calorie which is 1/100th part of the amount of energy required to raise one gram of water from 0° to 100° C. Barnes has shown the latter to be larger by 0.017 per cent. The 15° calorie is the one most commonly used. The kilogram calorie is very frequently employed in expressing heats of reaction and is equal to one thousand 15° calories. On account of the interrelation between the various forms of energy, it is quite customary to express a quantity of heat in other units besides the calorie.

1 cal. = 4.182 × 10^7 ergs.
1 cc. atmos. = 0.02423 cals.
1 volt coulomb = 1 joule = 10^7 ergs.

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[1] *Proc. Am. Acad.*, Nos. 1880 81.
[2] *Phil. Trans.*, **184**, 361 (1893)
[3] *Proc. Roy. Soc.*, **67**, 238 (1900).

These constants are those given by Lewis[1] from a critical survey of the literature.

REACTIONS AT CONSTANT VOLUME AND CONSTANT PRESSURE

When a chemical reaction takes place without volume change, such as the heat of combustion determined in a bomb calorimeter, the increase in the internal energy of the system, ΔU, is called the heat of reaction at constant volume. ΔU for any reaction is defined as the difference between the total internal energy of the resultants and the reactants. Under these conditions no external work is done by the system during the reaction.

In most cases, however, the reaction is carried out at constant pressure and the heat effect measured is slightly different from ΔU. The heat of reaction in a constant pressure calorimeter will be termed ΔH and is defined as the heat absorbed by the reacting system during the reaction. There is a difference in usage regarding the algebraic sign of the heat of reaction. When heat is evolved by our convention, the sign is negative, which corresponds to thermodynamic custom.

In most reactions involving solids or liquids the difference between ΔU and ΔH is negligible, but in cases where gases are concerned, this is not so. Since the heat content of a perfect gas is independent of the pressure, $\Delta H - \Delta U$ must be equal to the work done when the reaction takes place at constant pressure. If the reaction proceeds with the formation of 1 mol. of gas, work has to be done against the external pressure; this can usually be calculated with sufficient accuracy by assuming that the gases obey the law $PV = RT$. ΔH and ΔU measure the heat absorbed in the reaction from the surroundings, and since, if at constant pressure a gas is produced, work is done by the system on the surroundings, an additional quantity of heat equal to the work done must therefore be absorbed.

$$\Delta H = \Delta U + RT.$$

The decrease in energy content of a substance attending any change in state is given by the difference between the heat absorbed and the work done. In general, if Δn is the number of mols. of gas produced by the reaction less the number consumed, then

$$\Delta H = \Delta U + \Delta nRT. \qquad (1)$$

When the result is expressed in calories, $R = 1.9885$. For 18° C.

$$\Delta H = \Delta U + 580\Delta n. \qquad (2)$$

The combustion of benzoic acid takes place in accordance with the equation

$$C_6H_5COOH + 15(\tfrac{1}{2}O_2) = 7CO_2 + 3H_2O + 77{,}214 \text{ cals.}$$

For this reaction $n = -\frac{1}{2}$ and at 20° C.

$$\begin{aligned}\Delta H_{293} &= -77{,}214 - \tfrac{1}{2} \times 583,\\ &= -77{,}505 \text{ cals.}\end{aligned}$$

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[1] *J. Am. Chem. Soc.*, **35**, 1 (1913).

ΔH is the quantity commonly used in thermochemical work since it is the one most readily measured. It also renders unnecessary the evaluation of volume changes accompanying change of state and, as will be seen later, it is a quantity closely related to the change in free energy accompanying a reaction.

METHODS OF CALORIMETRY

Measurements of the heat effects accompanying chemical reactions are made in calorimeters and are determined from the change in temperature of the calorimeter and a knowledge of its heat capacity. The accuracy of the determination depends on the degree of precision attainable in these individual measurements.

The apparatus usually consists of the calorimeter proper, in which the reaction takes place, surrounded by an outer jacket with an air space between the two. The calorimeter is usually made of pure copper, nickel plated and polished in order to reduce radiation to a minimum.

Temperature Measurement: Various methods are employed for measuring the change in temperature of the calorimeter during the reaction. The simplest is to use an accurately calibrated Beckmann thermometer which can be read with an accuracy of about two parts in a thousand so that for a rise of 2° C. the minimum error would be 0.2 per cent. For more accurate work or for measuring smaller changes of temperature, many observers have used resistance thermometers[1] or multiple junction thermo-couples.[2] With these instruments an accuracy ten times that of the Beckmann thermometer can be obtained, but they necessitate expensive equipment and more labor in making observations.

Thermal Leakage: The greatest difficulty encountered in precise calorimetric work is due to thermal leakage. Many interesting and ingenious devices have been designed to overcome this difficulty. The chief error is due to the determination of the *total* temperature change brought about by the reaction. This is made up of two parts: the actual change observed directly and the heat which may leak to or from the calorimeter. As has been shown in the preceding paragraph, the error in measuring the observed change can be reduced to a negligible amount. Error in allowing for the thermal leakage effect may be due to a number of causes, such as the measurement of the thermal head, measurement of the rate of change of temperature, changes in the leakage constant of the calorimeter with varying temperature, lags, heat of stirring, evaporation, and leakage along metal connections to the calorimeter.

The interchange of heat between a calorimeter and its surroundings is practically proportional to the temperature difference, except for effects due to evaporation, convection and radiation. In a well-designed calorimeter four fifths of the heat transfer between the calorimeter and jacket is due to air conduction and convection, one fifth to radiation and a very small amount to evaporation. Richards and Burgess[1] found, with an open calorimeter. that when the temperature of the environment was slightly higher than that of the calorimeter (0.1°), there was, in 20 minutes, a barely noticeable change in the temperature of the calorimeter; but, when it was 0.1° lower, a noticeable cooling took place, probably due to distillation of water from the calorimeter and its condensation on the walls of the jacket. The evaporation of 10 mg. water consumes 6 cals., so that, in a determination involving 1000 cals., this introduces a variation of 0.6 per cent. Observations with an open calorimeter show that a rate of evaporation of 10 mg. per minute is not unusual and this involves a heat loss which is very uncertain. In all precision work the calorimeter should be closed with a close-fitting thin metal cover to check evaporation. The outside of the calorimeter vessel should be carefully dried and precautions taken against moisture absorbed on the outer surface.

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[1] Dickinson and Mueller, *Bull. Bur. Standards*, **3**, 641 (1907).

[2] White, *J. Am. Chem. Soc.*, **34**, 2292 (1914).

There are two distinct methods employed in calorimetry for successfully controlling thermal leakage: the one consists in keeping the temperature of the outer jacket constant, and the other or adiabatic method[2] in keeping the environment at every instant at the same temperature as the calorimeter. This is done either by electrically heating the outer jacket or by using the heat developed by some chemical reaction such as neutralization. The adiabatic method does not diminish error simply by reducing the magnitude of the thermal leakage loss. It does however permit the use of a large air gap if the calorimeter is closed, with a consequent reduction in the leakage constant of the calorimeter. With rapid changes of temperature, the use of a wide air gap may give rise to convection currents, since the temperature of the jacket always lags behind that of the calorimeter, due to a lag in the thermometer itself and to experimental difficulties. The adiabatic method[3] is quite often more convenient for practical use. Automatic devices have been developed for controlling the jacket temperature and keeping conditions adiabatic.[4] The differential hydrogen thermometer of Osgood regulated the temperature of the environment within 0.003° of that of the calorimeter.

In a calorimeter with a constant temperature environment, the width of the air space between the calorimeter and jacket is important. Too small an air gap means an insufficient amount of insulation around the calorimeter. The increase of insulation due to widening the gap may be considerable at first but soon reaches a maximum point beyond which the leakage rate increases due to the effect of convection currents. The problem of securing a constant ratio of thermal leakage to temperature is, practically, the problem of diminishing convection. The optimum width, according to White,[5] lies between 10 and 17 mm. With large calorimeters, where the temperature change is less, wider gaps may be used. The supports between the calorimeter and the jacket should be metallic[1] and the contact with the calorimeter as small as possible.

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[1] *J. Am. Chem. Soc.*, **32**, 431 (1910).

[2] Richards, Henderson, Frevert, *Z. physik. Chem.*, **59**, 532 (1907).

[3] For a discussion of adiabatic calorimetry see White, *J. Am. Chem. Soc.*, **40**, 387, 1890 (1918).

[4] Richards and Davis, *J. Am. Chem. Soc.*, **39**, 344 (1917). Richards and Osgood, *ibid.*, **37**, 1718 (1915).

[5] *J. Am. Chem. Soc.*, **40**, 379 (1918).

Dickinson made a comparison between the two methods by determining the heat capacity of a calorimeter and his results agreed within one part in fifteen thousand.

Calculating Thermal Leakage Effects: For the simpler methods of calorimetry, where the greatest precision is not desired, the graphic method of Jaeger and Steinwehr[2] is very useful in calculating thermal leakage effects.

The temperature of the calorimeter is noted at regular (30 sec.) intervals for a period of time before the reaction is started and the change should be directly proportional to the time. At a definite moment, at which the temperature prevailing can be readily calculated, the reaction is started, temperature readings still being taken as previously. The temperature changes at first rapidly, then more slowly, and finally a time is reached where the change is once more proportional to the time. By applying Newton's Law of Cooling, which states that the thermal leakage is proportional to the difference in temperature between the calorimeter and its environment, the maximum temperature which the calorimeter would have attained without thermal leakage can easily be calculated.

The observed calorimeter temperatures T are plotted as a function of time t. If T_0 is the temperature of the environment and K the leakage modulus or cooling constant for the calorimeter, then, from Newton's Law of Cooling,

$$\frac{dT}{dt} = -K(T - T_0). \qquad (3)$$

K is the temperature change of the calorimeter in unit time when the difference in temperature of the calorimeter and environment is 1° C. K can be calculated from the observations made before or after the reaction takes place. Newton's law only holds accurately for small temperature differences and therefore the smaller $(T - T_0)$ is, the more accurately the cooling correction can be estimated. If $\frac{dT}{dt} = v$, then, for the period before the reaction started,

$$v_1 = -K(T_1 - T_0) \qquad (4)$$

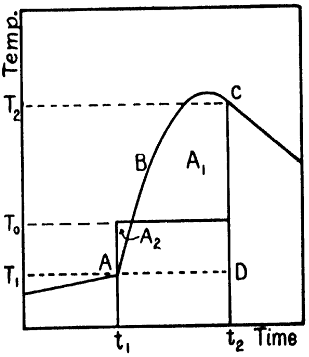

FIG. 2. Typical Temperature-time Curve in Calorimetry

and, for the period after the reaction,

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[1] See Dickinson, *Bull. Bur. Standards*, **11**, 210 (1914).

[2] *Ann. Physik*, **21**, 23 (1906).

$$v_2 = -K(T_2 - T_0); \tag{5}$$

hence

$$K = -\frac{1}{T_2 - T_1}(v_2 - v_1), \tag{6}$$

$$T_0 = \frac{v_1}{K} + T_1 = \frac{v_2}{K} + T_2. \tag{7}$$

The correction to the observed temperature difference, which has the opposite sign to the heat absorbed or given out by the calorimeter between the times t_1 and t_2, is given by the equation

$$T' = K\int_{t_1}^{t_2}(T - T_0)dt. \tag{8}$$

If the temperature T is plotted against time t in Fig. 3, then

$$\int_{t_1}^{t_2}(T - T_0)dt \tag{9}$$

is the difference of the areas A_1 and A_2 above and below T_0. The times t_1 and t_2 can be chosen at any optional points in the periods before and after the reaction. To the difference $T = T_2 - T_1$ where T_2 and T_1 correspond to the times t_2 and t_1 must be added the quantity T'.

The following example will illustrate the method.

Period before Reaction			Reaction Period			Period after Reaction		
Time	Temp.	ΔT	Time	Temp.	ΔT	Time	Temp.	ΔT
0	18.042°	+ 0.015	10			20	21.970°	− 0.027
1	.057	.016	11	19.8°	+ 1.2	21	.943	.026
2	.073	.015	12	21.0	0.7	22	.917	.026
3	.088	.014	13	21.7	0.2	23	.891	.026
4	.102	.016	14	21.9	0.1	24	.865	.026
5	.118	.013	15	22.01	0.03	25	.839	.027
6	.131	.014	16	22.04	+ 0.00	26	.812	.026
7	.145	.015	17	22.04	− 0.02	27	.786	.026
8	.160	.013	18	22.018	− 0.022	28	.760	.025
9	.173		19	21.996	− 0.026	29	.735	

The mean thermal leak for the first 9 mins. is

$$\frac{18.173 - 18.042}{9} = 0.0146° \text{ per min.}$$

The temperature at the beginning of the 11th min., when the reaction started, is best calculated by extrapolating each observed temperature to the beginning of the 11th min. and taking the average.

$$\frac{T_0 + 10v_1 + \cdots + T_9 + v_1}{10} = 18.189°,$$

where the subscripts to the T's refer to the times when readings are made. The thermal leak v_1 corresponds to a mean temperature of

$$\frac{18.173° + 18.042°}{2} = 18.107° = T_1.$$

At the end of the 19th min. the thermal leak is again practically constant and for the last ten minutes amounts to $\frac{21.710° - 21.970°}{10} = -0.0260°$ per minute $= v_2$, which in turn corresponds to a mean temperature of $T_2 = 21.840°$. By equation (6) $K = 0.0109$ and from equation (7) $T_0 = 19.45°$. For any temperature T the thermal leak is, accordingly, $(T - 19.45°) \times 0.0109$ degree per min. If the mean temperature for each minute is calculated, the thermal leak for that minute can be determined, and, by summing these terms, the equation for T' can be integrated.

Time	Mean Temp.	Thermal Leak
11th min.	19.0 °	− 0.45 × 0.0109
12 "	20.4	+ 1.0 "
13 "	21.4	+ 2.0 "
14 "	21.8	+ 2.4 "
15 "	21.95	+ 2.50 "
16 "	22.02	+ 2.57 "
17 "	22.04	+ 2.59 "
18 "	22.03	+ 2.58 "
19 "	22.01	+ 2.56 "
20 "	21.98	+ 2.53 "

$$T' = +20.3 \times 0.0109 = 0.221.$$

Without thermal leak, the final temperature would have been 21.970 + 0.221 = 22.191° and the temperature rise corresponding to the reaction would have been 22.191° − 18.189° = 4.002°.

T' can also be obtained by determining the area of the figure $ABCD$ in Fig. 2, subtracting from it the area of the rectangle $(T_0 - T_1)(t_2 - t_1)$ and multiplying this result by K. The approximate arithmetic method of integration employed in the calculation is however exact enough for the purpose.

Stirring: The satisfactory stirring of the calorimeter liquid is very important and has been neglected by many investigators. The stirrer should be so designed that, when working efficiently, it does not cause a change in temperature exceeding 0.001° per minute. Richards and Burgess[1] adopt a reciprocating stirrer made of two platinum rings, 2 cm. wide and perforated with holes; platinum rods supported these and were fastened to glass tubes. It was necessary to work this stirrer 60 times per minute to obtain adequate stirring. Dickinson[2] found a screw propeller better than the reciprocating

[1] *J. Am. Chem. Soc.*, **32**, 431 (1910).

[2] *Bull. Bur. Standards*, **11**, 210 (1914).

stirrer. With the latter, temperature differences of 0.5° were observed during the first minute after the heating current was turned off and these only reduced to 0.001° after 7 to 10 mins. The former showed 0.07° differences after the first minute, and these reduced to 0.001° in five minutes. MacInnes and Braham,[1] using an adiabatic arrangement, found that, if the temperature of the outer jacket were kept 0.15° below that of the calorimeter, there was no correction due to stirring.

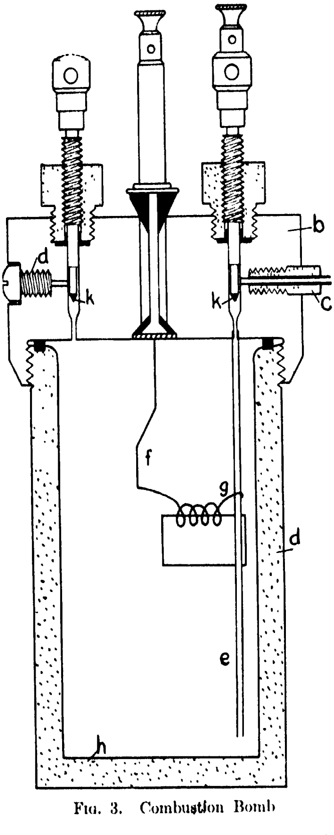

Fig. 3. Combustion Bomb

Heat Capacity of the Calorimeter: This corresponds to the amount of energy that is necessary to raise the temperature of the calorimeter 1° C. It is best measured by dissipating a known amount of electrical energy in the calorimeter and noting the rise in temperature. This method is due to Jaeger and Steinwehr.[2]

The Combustion Bomb: The bomb calorimeter was developed by Berthelot[3] to measure the heats of combustion of organic compounds. Atwater and Snell[4] have modified Berthelot's bomb in some respects, using a gold-plated copper lining in place of platinum. The bomb itself is made of gun metal steel, the cover is heavily threaded and screws down on to a lead washer. The material is suspended in a platinum dish in the bomb and oxygen is admitted to a pressure of about 25 atmospheres. Ignition is brought about by means of a weighed piece of iron wire which is heated electrically. Before ignition of the substance under investigation, the bomb is placed in a calorimeter and the heat evolved is measured in the usual way.

Richards[5] claimed that the lead washer was oxidized during the reaction and he covered it with gold foil to prevent this. By immersing the bomb in an adiabatic calorimeter, results were obtained on the combustion of cane sugar with an accuracy of 0.1 per cent. It was necessary to correct for the electrical energy used to heat the wire, the combustion of the iron, and the nitric acid formed by the oxidation of some of the nitrogen contained in the bomb. In a typical measurement, the total rise amounted to 1.605°, the correction for the burnt iron to − 0.015° and for the nitric acid to − 0.003°. When liquids are to be used, they are enclosed in glass or collodion bulbs and a known amount of sugar is added, which, on ignition, breaks the bulb, volatilizes the liquid and maintains sufficient heat for complete combustion.

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[1] *J. Am. Chem. Soc.*, **39**, 2110 (1917).
[2] *Verh. deut. phys. Ges.*, **5**, 50 (1903). *Z. physik. Chem.*, **53**, 153 (1905).
[3] *Ann. chim. phys.*, (5) **23**, 160 (1881); (6) **10**, 433 (1887).
[4] *J. Am. Chem. Soc.*, **35**, 659 (1903).
[5] *Z. physik. Chem.*, **59**, 535 (1907).

Dickinson[1] gives a critical study of combustion calorimetry, using a constant temperature jacket and a platinum resistance thermometer. He includes a complete bibliography on heats of combustion and general calorimetry. Robertson and Garner[2] have developed a calorimeter for determining the heat produced when high explosives are detonated, in order to obtain a measure of the energy developed and also to investigate the nature of the gases evolved. The bomb was made from vanadium steel and the walls and bottom were lined with steel to prevent damage to the bomb from flying fragments. To avoid loss of gas at the instant of explosion the thread of the steel plug was filled with a mixture of litharge and glycerine. The high explosive and detonator were contained in a steel cylinder suspended in the middle of the bomb.

Electrical Calorimeter: A very convenient form of calorimeter for many purposes was used by U. Fischer[3] in his work on silver iodide. It consists of a large well-evacuated Dewar vessel (A) having an easily removable wooden cover (B) carrying a stirrer (C), Beckmann thermometer and electrical heating coil (D). The heat capacity of the calorimeter can

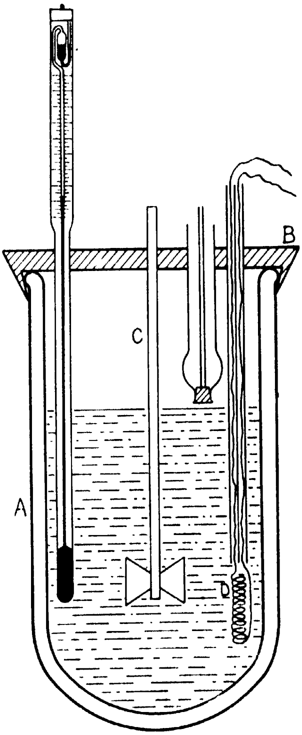

Fig. 4. Electrical Calorimeter

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[1] *Loc. cit.*

[2] *Proc. Roy. Soc.*, **103A**, 539 (1923).

[3] *Z. anorg. Chem.*, **78**, 57 (1912).

be determined by supplying, electrically, the same amount of heat as that generated by the reaction and over a similar period of time as that taken by the experiment, so that errors due to thermal leakage are similar to those occurring during the reaction. If a current of i amps. is passed for t seconds, and the resistance of the heater is r, and the rise in temperature produced is T_1 and if the reaction studied causes a rise of T_2, then q, the heat evolved by the reaction, is given by the expression

$$q = i^2 \cdot r \cdot t \times 0.2394 \frac{T_2}{T_1} .$$

The advantages of this method are great in work which does not require the highest precision; the diminution in thermal leakage with less care exercised as to thermal head is a great gain. Free evaporation is always a factor in a calorimeter of this type.

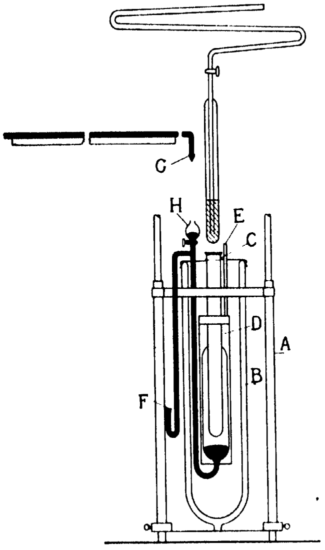

FIG. 5. Ice Calorimeter

Ice Calorimeter: Bunsen[1] was the first to use the decrease in volume when ice melts in order to measure heats of reaction, and, since his time, it has been used by a number of workers. Fig. 5 is the diagram of apparatus used by Marshall and Keyes[2] in work on the heat of adsorption of oxygen on charcoal. The entire calorimeter was contained in a support sliding on two vertical steel rods, and could be clamped in position at any height. This was necessary as the quartz tube containing the charcoal was fixed in position. The calorimeter proper was contained in a Dewar flask B, and was suspended by means of a collar and bracket at C, fitting the top of the inner tube and the top of the Dewar flask. The ice calorimeter, which was of the ordinary type, although made of pyrex glass, was surrounded by a glass tube D closed at the upper end by a rubber stopper, and open at the lower end. By blowing on the small tube E, the water could be forced out of the glass mantle, and the calorimeter surrounded by a jacket of air. This device is due to Boys,[3] and was quite effective in cutting down the natural leak of the apparatus. The capillary tube on which the volume changes were measured was broken by a

[1] *Pogg. Ann.*, **141**, 1 (1870).

[2] Private communication.

[3] *Phil. Mag.*, (5) **24**, 214 (1887).

ground joint at *F* and *G*. The horizontal tube was so arranged that the parts of the joint just came together when the calorimeter was raised in position. No lubricant was used on this joint. A small mercury reservoir at *H* enabled adjustment to be made of the preliminary position of the mercury column. Ice of good quality was used in the apparatus, and was ground to the consistency of snow in an ice shaver. This ice was then packed carefully between the Dewar flask and the Boys mantle. The packing had to be carefully done, otherwise, the ice calorimeter would not give a constant leak for any great length of time. The ice mantle was formed on the walls of the inner tube by partly filling the inner tube with mercury, and immersing in the mercury a glass tube containing a small amount of liquid ammonia. By keeping the mercury moving up and down by means of this inner ammonia tube, a very even mantle could be obtained. The ammonia gas was prevented from coming in contact with ice in the Dewar flask by leading it away through a stopper and a long rubber tube. With this apparatus a natural leak of .02 to .04 cm. on the scale per 5 mins. was obtained. This leak was dependent upon the purity of the ice used, and the difference in level between the horizontal capillary and the mercury level in the body of the calorimeter. These two effects operated in opposite directions, so that, by adjusting either, a point could be reached where no leak was noticeable. It was found that new additions of gas could be made about every hour, this being the time necessary to attain equilibrium. The amounts of heat measured each time were of the order of 0.5 to 2 small calories. After some 5 hours, the leak increased rapidly, with the result that only about 5 accurate readings could be obtained per run.

The great advantage of the ice calorimeter is that it can be used to measure very slow reactions with the same accuracy as that obtained in other methods of calorimetry. It is also suited for reactions where a very small amount of heat is evolved. It has been so used by Ramsay and Shields[1] and, quite recently, by Foresti,[2] in the measurement of heats of adsorption.

A typical measurement by Ramsay and Shields will illustrate the method of working. In their capillary, 1 mm. corresponded to 0.1053 cal. In an experiment, 9.744 g. Pt black absorbed 7.38 cc. hydrogen, the mercury column being displaced 43.6 mm. to the left corresponding to 4.591 cals. evolved or 13,930 cals. per mol. of hydrogen absorbed.

An accuracy of at least 1 per cent was obtained with this method. Some workers have preferred weighing the mercury rather than measuring the distance it moves along the capillary. It has however been found difficult to obtain reproducible results, as the mercury column does not always break off at the same point when the weighing bottle is removed. It is also a very tedious method. The chief objection to the capillary tube method is the probability of error through "sticking." If the tube is clean and is tapped carefully before reading, very little error can be detected.

One of the chief objections to the use of the ice calorimeter for work of precision is that the density of ice is not constant. Nichols[3] gives 0.91616 ± 0.00009 for the density of ice while Vincent[4] gives 0.9160. Leduc,[5] taking extreme precautions to get rid of all traces of dissolved air, found a value of 0.9176. He considered that water which had been boiled still contained 1 cc. of gas dissolved per liter at atmospheric pressure.

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[1] *Z. physik. Chem.*, **25**, 657 (1898)

[2] *Gazz. chem ital.*, **53**, 487 (1923).

[3] *Phys. Rev.*, **8**, 29 (1899).

[4] *Phys. Rev.*, **15**, 29 (1902).

[5] *Compt. rend.*, **142**, 149 (1906).

Continuous Flow Calorimeters: The continuous flow principle of calorimetry which was developed by Callendar and Barnes [1] for measuring specific heat has been more recently used by Keyes [2] for determining heats of neutralization. It can be adapted to any temperature at which thermostats can be successfully operated and an accuracy of 0.1 per cent can be attained. The two liquids which react are led into the mixing calorimeter through coils of silver tubes immersed in a thermostat controlled to 0.001°. The rates of flow are adjusted to give exact neutrality. The liquids enter the calorimeter at *A* and are completely mixed by the baffles *C* and *E* and then pass over the thermometer *F*. The calorimeter is vacuum jacketed and the heat loss varies from 2–6 per cent, depending on the rate of flow. By assuming Newton's Law of Cooling the heat loss can be calculated, and, from a knowledge of the specific heat of the salt solution, a calculation can be made for the heat of neutralization.

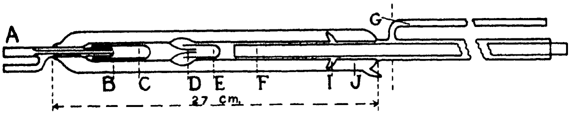

Fig. 6. Continuous Flow Calorimeter

Barry [3] has made a very exhaustive study of a method for determining the heat evolved by a very slow reaction such as the inversion of sugar. The adiabatic calorimeter developed has a gain or loss of half a gram-calorie in 10 hours.

Law of Constant Heat Summation

All the calculations made in thermochemical work are based on the law of the conservation of energy. Any system in a given condition has a definite heat content H determined by the state of the system, and the change in heat content ΔH due to any change in state depends solely on the initial and final states. ΔH is the quantity which is determined in the ordinary constant pressure calorimeter and is called the *heat of reaction*. Hess [4] pointed out that the heat evolved in a chemical reaction is independent of the method by which the reaction is made to take place. This principle is known as Hess' Law of Constant Heat Summation and is readily seen to be a corollary of the law of conservation of energy; Hess, however, did his work at a time when the first law was not generally accepted. It is very useful in calculating heat effects attending chemical changes that are not subject to our methods of calorimetry.

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[1] *Trans. Roy. Soc.* (Lond.), **199A**, 55 (1902).

[2] Keyes, Gillespie and Mitsukuri, *J. Am. Chem. Soc.*, **44**, 709 (1922).

[3] *J. Am. Chem. Soc.*, **42**, 1295, 1911 (1920); **44**, 899 (1922).

[4] *Pogg. Ann.*, **50**, 385 (1840).

Thermochemical Equations: In order to express changes in heat content of a system due to physical or chemical change at constant temperature and pressure, chemical equations are employed in which the chemical symbols denote the stoichiometrical amounts of the substances involved and also the respective heat contents of these substances.

$$H_2\,(g) + I_2\,(s) = 2HI\,(g); \qquad \Delta H = 12{,}200 \text{ cals.}$$

Here

$$\Delta H = H_{2HI\,(g)} - (H_{H_2\,(g)} + H_{I_2\,(s)}).$$

The state of aggregation is designated in a thermochemical equation by attaching to the formula the letters (*s*), (*l*), or (*g*). If one of the reactants is dissolved in water, this fact is shown by giving the number of mols. of water per mol. of reactant. If sufficient water is present so that further addition produces no appreciable heat effect, the symbol (aq) is written in the equation

$$NH_3\,(aq) + HCl\,(aq) = NH_4Cl\,(aq), \qquad \Delta H = -\ 12{,}300 \text{ cals.}$$

Thermochemical equations may be treated algebraically and added to or subtracted from one another.

$$C_2H_4\,(g) + 3O_2\,(g) = 2CO_2\,(g) + 2H_2O\,(l); \quad \Delta H = -\ 342{,}000 \text{ cals.} \quad (a)$$
$$2C\,(\text{Graphite}) + 2O_2\,(g) = 2CO_2\,(g); \quad \Delta H = -\ 188{,}000 \text{ cals.} \quad (b)$$
$$2H_2\,(g) + O_2\,(g) = 2H_2O\,(l); \quad \Delta H = -\ 136{,}000 \text{ cals.} \quad (c)$$

Adding (*b*) and (*c*) and subtracting (*a*), we have

$$2C\,(\text{Graphite}) + 2H_2\,(g) = C_2H_4\,(g); \qquad \Delta H = 18{,}000 \text{ cals.}$$

or alternatively

$$C_2H_4\,(g) = 2C\,(\text{Graphite}) + 2H_2\,(g); \qquad \Delta H = -\ 18{,}000 \text{ cals.}$$

When 24 g. of graphite react with 4 g. of hydrogen to form 28 g. of ethylene gas, 18,000 cals. of heat energy are absorbed.

By this method, ΔH may be calculated for reactions where it is impracticable to make a direct measurement. The results obtained when a considerable number of reactions are combined do not possess a high degree of accuracy, since the absolute error of the final result is the sum of the absolute errors of all the determinations considered and may give a very high percentage error.

Heats of Formation: The absolute heat content of any element is unknown and in thermochemical work we deal only with differences; yet it is convenient, for purposes of tabulation, to adopt a standard reference state for each element so that values can be assigned for the heat content of compounds. The heat content has been taken as zero for all elements in the form stable at room temperature. We then speak of the ΔH of a substance, meaning the increase in heat content when that substance is formed from its elements in their standard state. For C_2H_4, $\Delta H = 18{,}000$ cals.

From a table of heat contents, the heat change in any chemical reaction can be calculated by subtracting the sum of the heat contents of the resultants from that for the reactants.

The following example will show the application of the principles discussed above: To find the heat of formation of sulphuric acid from its elements.

$SO_2\ (g) + aq = SO_2\ aq; \quad \Delta H = -\ 8{,}000$ cals. (*a*)
$H_2SO_4\ (l) + aq = H_2SO_4\ aq; \quad \Delta H = -\ 18{,}000$ cals. (*b*)
$\frac{1}{2}H_2\ (g) + \frac{1}{2}Cl_2\ (g) = HCl\ (g); \quad \Delta H = -\ 22{,}000$ cals. (*c*)
$HCl\ (g) + aq = HCl\ aq; \quad \Delta H = -\ 17{,}300$ cals. (*d*)
$S\ (s) + O_2\ (g) = SO_2\ (g); \quad \Delta H = -\ 70{,}200$ cals. (*e*)
$H_2\ (g) + \frac{1}{2}O_2\ (g) = H_2O\ (l); \quad \Delta H = -\ 68{,}400$ cals. (*f*)
$Cl_2\ (g) + SO_2\ aq + 2H_2O\ (l) = H_2SO_4\ aq + 2HCl\ aq; \quad \Delta H = -\ 73{,}900$ cals. (*g*)
From (*c*) and (*d*), $\Delta H_{HCl\ aq} = -\ 39{,}300$ cals. (*h*)
From (*a*) and (*e*), $\Delta H_{SO_2\ aq} = -\ 78{,}200$ cals. (*i*)
From (*f*), (*g*), (*h*) and (*i*), $\Delta H_{H_2SO_4\ aq} = -\ 210{,}300$ cals. (*k*)
From (*b*) and (*k*), $\Delta H_{H_2SO_4\ (l)} = -\ 192{,}300$ cals.

Thus, by the use of Hess's law, we have found the heat of formation of 98 g. sulphuric acid from 2 g. hydrogen, 32 g. sulphur and 64 g. oxygen to be $\Delta H = -\ 192{,}300$ cals. The numerical values of heats of formation are those which will be found listed in tables of physical and chemical constants.

The following table will give the heats of formation of some typical inorganic compounds.

TABLE I

HEATS OF FORMATION OF TYPICAL COMPOUNDS

Reaction	ΔH at $T = 288°$ K.
$\frac{1}{2}H_2\ (g) + \frac{1}{2}Cl_2\ (g) = HCl\ (g)$	− 22,000
$\frac{1}{2}H_2\ (g) + \frac{1}{2}Br_2\ (l) = HBr\ (g)$	− 8,440
$\frac{1}{2}H_2\ (g) + \frac{1}{2}I_2\ (s) = HI\ (g)$	6,400
$\frac{1}{2}H_2\ (g) + \frac{1}{2}F_2\ (g) = HF\ (g)$	− 38,500
$H_2 + S$ (rhombic) $= H_2S\ (g)$	− 2,730
$\frac{1}{2}N_2\ (g) + \frac{3}{2}H_2\ (g) = NH_3\ (g)$	− 11,890
$Si\ (s) + 2H_2\ (g) = SiH_4\ (g)$	6,700
$\frac{1}{2}N_2\ (g) + \frac{3}{2}O_2\ (g) + \frac{1}{2}H_2\ (g) = HNO_3\ (l)$	− 41,600
$Na\ (s) + \frac{1}{2}I_2\ (s) = NaI\ (s)$	− 69,080
$2Na\ (s) + C\ (s) + \frac{3}{2}O_2\ (g) = Na_2CO_3\ (s)$	−270,800
$K\ (s) + \frac{1}{2}I_2\ (s) = KI\ (s)$	− 80,130
$Ca\ (s) + I_2\ (s) = CaI_2\ (s)$	−141,300
$Ag\ (s) + \frac{1}{2}F_2\ (g) = AgF\ (s)$	− 23,200
$Ag\ (s) + \frac{1}{2}Cl_2\ (g) = AgCl\ (s)$	− 29,940
$Ag\ (s) + \frac{1}{2}Br_2\ (l) = AgBr\ (s)$	− 23,900
$Ag\ (s) + \frac{1}{2}I_2\ (s) = AgI\ (s)$	− 15,000
$Pb\ (s) + Cl_2\ (g) = PbCl_2\ (s)$	− 83,900
$Pb\ (s) + Br_2\ (l) = PbBr_2\ (s)$	− 64,450
$Pb\ (s) + I_2\ (s) = PbI_2\ (s)$	− 41,850

Variation of Heat of Reaction with Temperature: Each heat of reaction is given for a definite temperature but this does not mean that the temperature has been constant throughout the reaction. In a combustion bomb the temperature may be very high at the moment of the combustion but the final temperature is only a few degrees different from the initial temperature. All we are concerned with is the initial and final state. For the applications of Hess's law, it is necessary for all the heats of reaction concerned to be calculated for a single temperature. Most of the calorimetric data in the literature are for a temperature of about 18° C. It is frequently required to know the heat of some particular reaction at another temperature and this can be readily calculated from a knowledge of the specific heats of the resultants and reactants of the reaction. Let ΔH_1 be the heat of reaction at temperature T_1 and ΔH_2 at T_2. Let us consider the following cyclical process: the reaction is carried out at T_1 with an absorption of heat ΔH_1 and the resultants of the reaction are heated to T_2 whereby an amount of heat $(T_2 - T_1)C''$ is absorbed, where C'' is the mean molal heat capacity of the resultants between T_1 and T_2; again, let us heat the reactants from T_1 to T_2 with an absorption of heat $(T_2 - T_1)C'$, where C' is the mean molal heat capacity of the reactants, and then carry out the reaction at T_2 with an absorption of heat ΔH_2. Then, by the First Law of Thermodynamics,

$$\Delta H_2 + C'(T_2 - T_1) = \Delta H_1 + C''(T_2 - T_1), \tag{10}$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C'' - C'. \tag{11}$$

When the difference between T_2 and T_1 becomes infinitesimal, this reduces to

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p, \tag{12}$$

where ΔC_p is the sum of the heat capacities of the resultants less that for the reactants or the total increase in heat capacity from the reaction. This equation was first deduced by Kirchoff.[1] The molal heat capacity of a substance is defined as

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \cdot$$

If it can be regarded as constant, we may define C_p as the heat required to raise one mol. of the substance one degree. If we have a curve plotting H against T for a substance, the tangent at any point will give the molal heat capacity for that particular temperature. Over a small range of temperature around room temperature C_p can be regarded as constant and

$$\Delta H_2 - \Delta H_1 = C_p(T_2 - T_1). \tag{13}$$

For the reaction,

$$2H_2\ (g) + O_2\ (g) = 2H_2O\ (g), \quad \Delta H_{291}^\circ = -116{,}115 \text{ cals.}$$

---

[1] *Ann. Physik*, (2) **103**, 177 (1858).

The molal heat capacities are as follows:

$$\begin{aligned} &H_2; && C_p = 6.818, \\ &O_2; && C_p = 6.960, \\ &H_2O; && C_p = 9.000. \end{aligned}$$

Hence, $\Delta C_p = -2.596$. For the interval 100° C. to 130° C.,

$$\Delta H_{403^\circ} - \Delta H_{373^\circ} = -2.596 \times 30 = -77.88 \text{ cals.};$$

hence

$$\Delta H_{403^\circ} = -116{,}193 \text{ cals.}$$

When we are dealing with rapid variations in heat capacity or large temperature ranges, an empirical equation can be set up to express the variation of heat capacity with temperature.

$$C_p = a + bT + cT^2 + \cdots, \tag{14}$$

where the number of terms will depend on the temperature range and the accuracy of the data. In dealing with a chemical reaction for each of whose members a heat capacity equation has been determined over a range of temperature,

$$\Delta C_p = a_0 + b_0 T + c_0 T^2 + \cdots, \tag{15}$$

where a_0 is the algebraic sum of all the a's, b_0 of all the b's and so on. By the use of this equation we are now in a position to integrate equation (12).

$$\Delta H = \Delta H_0 + a_0 T + \tfrac{1}{2} b_0 T^2 + \tfrac{1}{3} c_0 T^3 + \cdots, \tag{16}$$

where ΔH_0 is an integration constant and can be calculated from a single experiment.

Let us illustrate the usefulness of this method by calculating ΔH_{1273° for the reaction

$$H_2\,(g) + \tfrac{1}{2}O_2\,(g) = H_2O\,(g)$$

from the following data:

$$\begin{aligned} &(a) \quad H_2\,(g) + \tfrac{1}{2}O_2\,(g) = H_2O\,(l); && \Delta H_{293} = -68{,}400 \text{ cals.} \\ &(b) \qquad\qquad\quad H_2O\,(l) = H_2O\,(g); && \Delta H_{373} = 9670 \text{ cals.} \end{aligned}$$

The molal heat capacities at constant pressure of the gases involved are given by the equations:

$$\begin{aligned} &O_2\,(g); && C_p = 6.69 + 0.0007T, \\ &H_2\,(g); && C_p = 6.54 + 0.0007T, \\ &H_2O\,(g); && C_p = 8.81 - 0.0019T + 0.00000222T^2. \end{aligned}$$

For the reaction, $H_2O\,(l) = H_2O\,(g)$,

$$\Delta C_p = 9.19 - 0.0019T + 0.00000222T^2$$

and

$$\Delta H = \Delta H_0 - 9.19T - 0.00095T^2 + 0.00000074T^3.$$

Whence, at 100° C., $9670 = \Delta H_0 - 3428 - 132 + 38$; hence

$$\begin{aligned} &(c) \quad \Delta H = 13{,}192 - 9.19T - 0.00095T^2 + 0.00000074T^3, \\ &(d) \quad \Delta H_{293^\circ} = 10{,}439. \end{aligned}$$

Now, summing (*a*) and (*d*),

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g), \qquad \Delta H_{293} = -57{,}961,$$

and

$$\Delta C_p = -1.08 - 0.0029T + 0.00000222T^2,$$

and

$$\Delta H = -57{,}539 - 1.08T - 0.00145T^2 + 0.00000074T^3;$$

hence

$$\Delta H_{1273^\circ} = -59{,}738 \text{ cals.}$$

LATENT HEAT

The *heat of fusion* of solids, the *heat of vaporization* of liquids, and the *heat of transition* of one modification of a solid to another (such as red to yellow phosphorus) are important quantities that are frequently used in calculating heats of reaction and entropy values for pure substances. In nearly every case the transition of the form stable at the lower temperature into that stable at the higher temperature is accompanied by an absorption of heat.

Methods for Determining Latent Heat: A calorimeter of the unstirred type developed in Nernst's laboratory, which depends for its success on the rapid equalization of temperature throughout the calorimeter by means of conduction, has been designed at the Bureau of Standards[1] in connection with an investigation on refrigerants. With this aneroid calorimeter the heat of fusion of ice was determined as 1435.7 cals. per mol. The following table gives the latent heat of fusion of some substances.

TABLE II

HEATS OF FUSION

Substance	Cals./mol.	Temp.
Sulphur	299.8	115°
Benzene	2406	5.4
Zinc	1840	419
Lead	1214	327
Silver	2273	961
Mercury	565.7	– 39

In order to measure heats of vaporization of a liquid, one can determine either the amount of heat given up by a known amount of saturated vapor on condensing or the amount of heat required to turn a liquid into vapor at the same temperature. The first method was developed by Berthelot and improved by later workers[2] in this field. Smith[3] has developed the latter method for measuring the heat of vaporization of water; more recently, Fogler and Rodebush[4] have used it to determine the heat of vaporization of mercury. A gentle stream of air is drawn through a calorimeter whose temperature is kept constant by supplying heat electrically and the amount of liquid evaporated is weighed. By making two determinations at different rates but at the same temperature, the heat of vaporization can be calculated directly. Smith obtained a value of 9661 cals. for the molal heat of vaporization of water at 100° C., as compared with Henning's value of 9697 cals.

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[1] *Bull. Bur. Standards*, **12**, 23, 49 (1914); **14**, 133 (1918).

[2] Griffiths, *Phil. Trans.*, **A**, p. 261 (1895). Kahlenberg, *J. Phys. Chem.*, **5**, 215 (1901). Gunther Vogel, *Z. physik. Chem.*, **73**, 445 (1910). Henning, *Ann. Physik*, (4) **21**, 849 (1906).

[3] *Phys. Rev.*, **33**, 173 (1911).

[4] *J. Am. Chem. Soc.*, **45**, 2080 (1923).

The following table gives the molal heat of vaporization of a few substances at their boiling points.

TABLE III

HEATS OF VAPORIZATION

Substance	Cals./mol.	Temp.
Benzene	7596	80.1°
Bromine	3643	61
Iodine	3039	184
Nitrogen	1334	− 195.6
Oxygen	1631	− 182.9

If we assume that the simple gas laws apply to saturated vapors and that the specific volume in the liquid state is negligible compared to that of the vapor, we obtain an equation

$$\frac{dlnp}{dT} = -\frac{\Delta H}{RT^2}. \tag{17}$$

This is the Clapeyron-Clausius equation connecting the vapor pressure of a substance with its heat of vaporization.

Kahlbaum and Wirkner[1] found the following vapor pressures for benzene:

$$T_1 = 293°; \quad p_1 = 75.0 \text{ mm.},$$
$$T_2 = 303°; \quad p_2 = 118.0 \text{ mm.},$$

from which $\Delta H = 7990$ cals., as compared with an observed value of 8040 cals.

Equation (17) can be put in the form

$$-\frac{\Delta H}{T} = R\frac{dlnp}{dlnT} = R\frac{dln\pi}{dln\theta}, \tag{18}$$

where π and θ are the reduced temperature and pressure. From the theory of corresponding states, the last term should have the same value for all substances at corresponding states and Guldberg[2] has shown that for a large variety of substances the absolute boiling point is about $\frac{2}{3}$ of the critical temperature. Hence, it follows that the quotient of the molecular heat of vaporization and the absolute temperature of the boiling point must be approximately constant. This relationship is known as Trouton's Rule;[3] the constant lies between 20 and 22. This rule gives only a rough value and when applied to liquids over a wide range of boiling point the constant shows a marked trend.

[1] *Dampfspannkraftmessungen*, (2), page 17, Basel (1897).

[2] *Z. physik. Chem.*, 5, 374 (1890).

[3] *Phil. Mag.*, (5) 18, 54 (1884).

TABLE IV

Trouton's Rule Constants

Substance	T_b	ΔH	$\frac{\Delta H}{T_b}$
Helium	4.29	22	5.1
Hydrogen	29.4	214	10.5
Oxygen	90.6	1664	18.3
Ethyl ether	307	6466	21.1
Carbon bisulphide	319	6490	20.4
Methyl formate	304.8	6611	21.69
Chloroform	334.5	6972	20.84
Methyl alcohol	337.7	8383	24.83
Benzene	353.2	7370	20.87
Propyl formate	353.9	7945	22.45
Ethyl alcohol	351.2	9972	28.40
Ethyl propionate	372.2	8354	22.45
Water	373	9660	25.90
Formic acid	373.6	5541	14.83
Toluene	383.8	7994	20.84
Aniline	457	10602	23.20
Methyl salicylate	497	11000	22.2

Nernst[1] has developed this idea by employing Berthelot's equation of state in the derivation of the Clapeyron equation and obtains the equation

$$\Delta H = R\frac{d\ln p}{d\left(\frac{1}{T}\right)}\left(1 + \pi\frac{9}{128}T(1 - 6T^2) - \frac{v_0'}{v_0}\right), \tag{19}$$

where v_0' and v_0 are the molecular volume of the liquid and its saturated vapor and π is the reduced pressure. He states that, as a rule, the values of ΔH calculated by this equation are more accurate than those determined experimentally. Substances containing the hydroxyl group such as water, alcohol and organic acids, whose molecules in the liquid state are believed to be associated, form exceptions to the rule.

Hildebrand[2] showed that $\frac{\Delta H}{T}$ is the same for different substances if they are compared, not at the boiling points, but at temperatures where the liquids have the same vapor concentration. The pressure is low enough for the vapor to obey the gas laws.

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[1] *Z. Elektrochem.*, **22**, 185 (1916).

[2] *J. Am. Chem. Soc.*, **37**, 970 (1915).

TABLE V

HILDEBRAND'S CONSTANTS FOR $\frac{\Delta H}{T}$

Substance	$\frac{\Delta H}{T}$	Substance	$\frac{\Delta H}{T}$
Nitrogen	27.6	Zinc	26.4
Oxygen	27.6		
Hexane	27.2	Ammonia	32.4
Stannic chloride	27.2	Water	32
Mercury	26.2	Ethyl alcohol	33.4

A few determinations have been made on the heats of transition when a substance passes from one allotropic state to another and the following table gives some of the results obtained.

TABLE VI

HEATS OF TRANSITION

Substance	States	ΔH	
P_2O_5	Crystalline—glassy	−11700 cals.	
P	White—red	− 3700	
HgI_2	Yellow—red	− 3000	
AgBr	Pptd.—crystalline	− 3100	
AgI	Regular—hexagonal	− 1530	
Sn	White—grey	− 591	at 19° C.

SPECIFIC HEAT

The quantity of heat necessary to raise the temperature of 1 g. of a substance through 1° C. at any temperature is called the specific heat, c, of the substance at that temperature.

Specific Heat of Gases: The heat capacity of a gas varies according as it is measured at constant volume or constant pressure. If one gram-mol. of a substance is heated at constant pressure from temperature T to $T + dT$, the amount of heat consumed is $C_p \cdot dT$, where C_p is the molecular heat and is equal to Mc_p, M being the molecular weight. This heating can be considered as taking place in another way; the substance may first be heated at constant volume with an expenditure of heat $C_v dT$ and then allowed to expand at constant temperature to the original pressure whereby an amount of heat $\frac{\partial U}{\partial v} dv + pdv$ is required. Hence,

$$C_p dT = C_v dT + \left(p + \frac{\partial U}{\partial v}\right) dv \tag{20}$$

or

$$C_p - C_v = \left(p + \frac{\partial U}{\partial v}\right) \frac{\partial v}{\partial T} \cdot$$

If we are dealing with a perfect gas,

$$\frac{\partial U}{\partial v} = 0 \qquad \text{and} \qquad \frac{\partial v}{\partial T} = \frac{R}{p},$$

and so

$$C_p - C_v = R. \tag{21}$$

Molecular Heat at Constant Pressure: The difficulty in determining specific heats of gases is due to the fact that the mass of a given volume is relatively small and a large volume of gas must be used to obtain accurate results. The ordinary method of mixture has been applied successfully in determining specific heats of gases at constant pressure. The method most generally used consists in passing a known volume of gas heated to a definite temperature through a colder calorimeter and measuring the heat liberated. Delaroche and Berard[1] first used this method but Regnault[2] elaborated it, paying much attention to details. He was the first to obtain satisfactory results. Wiedemann[3] further improved the calorimeter by decreasing its size and obtaining a much quicker heat exchange between the gas and the walls of the vessel by filling the calorimeter with metal turnings. Holborn and Henning,[4] using this method, measured the specific heat of air, nitrogen and carbon dioxide up to 1400° C. The following table gives the specific heat of air at varying temperatures by several observers.

TABLE VII

SPECIFIC HEAT OF AIR

° C.	Regnault	Wiedemann	Holborn and Austin
0	0.1870	0.1952	0.2028
100	0.2145	0.2169	0.2161
200	0.2396	0.2387	0.2285
400	—	—	0.2502
600	—	—	0.2678
800	—	—	0.2815

A method already mentioned, due to Callendar, has been developed by Scheel and Heuse[5] which gives the specific heat over a very small temperature interval. The gas at a definite temperature flows into the calorimeter, is heated electrically and the rise in temperature measured by a resistance thermometer.

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[1] *Ann. Chim.*, **85**, 72 (1813).

[2] *Memoires de l'Institute de France*, 26 (1862).

[3] *Pogg. Ann.*, **157**, 1 (1876).

[4] *Ann. Physik*, **23**, 809 (1907).

[5] *Ann. Physik*, **37**, 79 (1912).

If i is the current, E the potential difference across the heating coil, dT the rise in temperature of the gas, Q the rate of flow of gas in grams per second, J the mechanical equivalent of heat and c_p the specific heat of the gas, then

$$Ei = Jc_pQdT + hdT, \tag{22}$$

where hdT is a term representing the heat losses. By experimenting with two rates of flow and adjusting the current to keep dT constant, the second term can be eliminated and c_p determined directly. Scheel and Heuse give the following figures for the molecular heat of dry, CO_2-free air at atmospheric pressure.

T	C_p
20° C.	6.98
− 78	7.05
−183	7.32

Molecular Heats of Gases at Constant Volume: Joly[1] has developed a method for determining specific heats of gases at constant volume; a metal vessel is suspended from a balance in a cavity through which a rapid current of steam can be admitted and its weight is determined. Steam is admitted and condenses on the cold vessel until it is heated to 100° C. Since the whole space is filled with steam, there is no heat loss and the amount of water condensed is a measure of the heat necessary to bring the vessel from its initial temperature to 100° C. If the vessel is first evacuated and then filled with gas, the difference between the two increments gives directly the quantity of heat necessary to heat the enclosed gas to 100° C.

Eucken[2] has used a slightly different method for work at low temperatures. Here the method is very accurate since the heat capacity of the vessel itself can be made very small; the vessel is heated electrically in a vacuum.

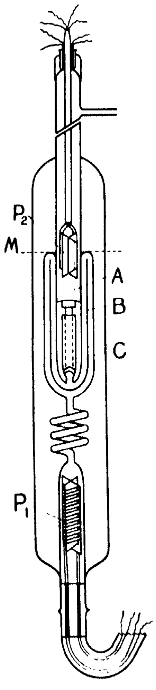

FIG. 7. Continuous Flow Calorimeter for Determining Specific Heat.

The Explosion Method: Bunsen, in 1867, first used the explosion method for determining specific heats at high temperatures. The combustible gas and oxygen are mixed with various indifferent gases, exploded in a closed bomb and the maximum pressure of the explosion measured. From this, one can calculate the maximum temperature attained and hence the heat capacity of the gaseous mixture, since the heat of reaction is known. Pier[3] and Bjerrum[4] have been recent workers in this field. Pier showed that previous workers had failed to measure the maximum pressure and he developed a sensitive membrane manometer consisting of a very thin steel plate with a high period of vibration. The deformation of the plate by the explosion could be recorded photographically. The chief source of uncertainty in results of explosion experiments lies in the estimation of the heat loss while the maximum pressure is being attained. From the maximum pressure P of the explosion, the temperature can be calculated by the equation

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[1] *Phil. Trans.*, **182**, 73 (1892).

[2] *Sitz.-ber. preuss. Akad. Wiss.*, 141 (1912).

[3] *Z. Elektrochem.*, **15**, 537 (1909); **16**, 897 (1910).

[4] *Z. physik. Chem.*, **79**, 513 (1912); **87**, 641 (1914).

$$\frac{T_2}{T_1} = \frac{P}{p \cdot \epsilon}, \tag{23}$$

where T_1 and T_2 are the initial and final temperatures, p the initial pressure, and ϵ the ratio of the number of molecules before to that after the explosion. Pier found, between 0° and 2350° C., $C_v = 2.977$ for argon. In the following table, the molecular heats at constant volume of a few gases are given.

TABLE VIII

C_v FOR SEVERAL GASES

Gas	Temp. in ° C.					
	0°	100°	200°	500°	1200°	2000°
Argon . . .	2.98	2.98	2.98	2.98	3.0	3.0
N_2, O_2, HCl, CO . . .	4.90	4.93	5.17	5.35	5.75	6.22
Cl_2	5.85	5.88	6.12	6.30	6.9	7.4
CO_2, SO_2	6.80	7.43	8.53	9.43	11.1	11.5
$(C_2H_5)_2O$	32	32.6	11.6			

At low temperatures, Eucken[1] found, for hydrogen,

$$\begin{array}{llllll} T° \text{ K.} = & 35° & 50° & 80° & 100° & 273° \\ C_v = & 2.98 & 3.91 & 3.14 & 3.42 & 4.84 \end{array}$$

and for helium

$$\begin{array}{lllll} T° \text{ K.} = & 18° & 22° & 26° & 30° \\ C_v = & 2.90 & 3.00 & 3.10 & 3.10 \end{array}$$

Indirect Methods for C_v: Since the direct determination of C_v for gases is very troublesome, several indirect methods have been worked out that give satisfactory results. The ratio of $\frac{C_p}{C_v}$ can be determined directly and several methods of attack have been employed.

Method of Clément and Désormes:[2] The gas under consideration is placed in a large container at a pressure P_1 which is slightly greater than atmospheric.

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[1] *Sitz.-ber. preuss. Akad. Wiss.*, 144 (1912).

[2] *Jour. de Phys.*, **89**, 321, 428 (1819).

The container is opened for a moment so that the internal pressure drops to atmospheric and then is quickly closed. While the gas in the container was expanding, it cooled slightly and on warming again the pressure increased to P_2. Let $P_1 = P + p_1$ and $P_2 = P + p_2$, where P is atmospheric pressure and p_1 and p_2 are small compared to P. If V is the volume of the container, then the amount of work done by the escaping gas is $V(p_1 - p_2)$. This work was done at the expense of the heat content of the gas, since we assume that the expansion takes place adiabatically. The amount $t°$ which the gas cooled during expansion can be calculated from the equation

$$\frac{t}{T} = \frac{p_2}{P}, \tag{24}$$

since the pressure rose from P to $P + p_2$, while the temperature changed from $T - t$ to T. The heating is done at constant volume so that the amount of heat consumed is

$$nC_vt = \frac{PV}{RT}C_vt = \frac{p_2V}{R}C_v. \tag{25}$$

Since this quantity is equivalent to the work done by the gas on expansion,

$$p_1 - p_2 = \frac{p_2}{R}C_v. \tag{26}$$

But we have shown that

$$C_p - C_v = R,$$

so

$$\frac{C_p}{C_v} = \frac{p_1}{p_1 - p_2} = \gamma. \tag{27}$$

By working with a large volume of gas and a small pressure difference, it is possible to minimize very greatly the loss of heat due to conduction during the expansion; the chief difficulty is in securing a quick equalization of pressure.

A somewhat better method is due to Lummer and Pringsheim.[1] They filled a vessel of 90 liters capacity with a gas at known temperature and at a pressure which exceeded atmospheric. The excess pressure was allowed to blow off through a large orifice and a complete equalization with atmospheric pressure was ensured. The temperature of the gas was now determined again quickly by a platinum resistance thermometer of very fine wire placed in the center of the flask. Since the process is adiabatic,

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{(\gamma-1)/\gamma}. \tag{28}$$

---

[1] *Wied. Ann.*, **64**, 582 (1898).

They obtained the following values:

Gas	γ	Gas	γ
Air	1.4026	Carbon dioxide	1.2995
Oxygen	1.3977	Hydrogen	1.4084

The Method of the Velocity of Sound Waves: This method depends on measurements of the velocity of sound in gases. The velocity of transmission of sound U in any gas is given by the expression

$$U = \sqrt{\frac{p}{d}\gamma}, \tag{29}$$

where d is the density of the gas.

The ratio of the velocity in two gases, both at the same pressure, is

$$\frac{U_1}{U_2} = \sqrt{\frac{\gamma_1 d_2}{\gamma_2 d_1}} \tag{30}$$

or, since, at constant temperature, the densities are proportional to the molecular weights,

$$\frac{U_1}{U_2} = \sqrt{\frac{\gamma_1 M_2}{\gamma_2 M_1}}. \tag{31}$$

The ratio of the velocity of sound in any two gases can be determined very accurately by a method developed by Kundt.[1]

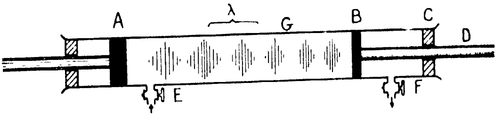

FIG. 8. Kundt's Tube for Measuring Velocity of Sound in a Gas

The tube G in Fig. 8 is fitted with a plunger B and a glass rod D. A small amount of finely ground cork or lykopodium powder is spread in the bottom and the tube filled with the gas under consideration. A piece of moist cloth is rubbed along the tube D, causing it to emit a shrill note. The gas in the tube takes up these vibrations and the waves are made visible by the powder. By moving B up and down the tube a position is found where the stationary waves are sharply defined and by measuring the distance between two nodal points a quantity l is obtained which is directly proportional to the velocity of sound in the gas under consideration.

The value for γ in air has been found to be 1.403. When l for air has been determined by this method, it is possible to determine γ for any gas.

$$\gamma = 1.403 \frac{Ml_1^2}{29.0 l_2^2}, \tag{32}$$

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[1] *Pogg. Ann.*, **127**, 497 (1866); **135**, 337, 527 (1868).

where l_1 and l_2 are the nodal distances for the gas and for air under the same conditions of temperature and pressure.

The following table gives values for γ for a number of gases.

TABLE IX

$\frac{C_p}{C_v} = \gamma$ FOR SEVERAL GASES

Substance	γ	Substance	γ
Argon	1.66	Nitric oxide	1.40
Mercury	1.66	Carbon dioxide	1.26
Hydrogen	1.41	Ether	1.06
Chlorine	1.30		

Specific Heat of Liquids: The specific heats of liquids and solutions have been determined with the aid of the continuous flow method of Callendar and Barnes and also by measuring the heat rise in a Dewar vessel when the system is heated electrically. The difficulty of the latter method is in determining the heat capacity of the calorimeter. Richards and Rowe[1] have measured the specific heat of hydrochloric acid solutions, using an adiabatic calorimeter.

TABLE X

SPECIFIC HEATS OF HYDROCHLORIC ACID SOLUTIONS

Composition of Solution	c_p	Composition of Solution	c_p
$HCl + 10H_2O$	0.752	$HCl + 100H_2O$	0.9634
" $+ 20$	0.849	" $+ 200$	0.9812
" $+ 25$	0.8776	" $+ 400$	0.9905
" $+ 50$	0.9320		

Goodwin and Kalmus[2] have measured the specific heats of a number of inorganic salts at a temperature just above their melting point.

TABLE XI

MOLAR HEAT CAPACITIES OF FUSED SALTS

Salt	T° C.	C_p
KNO_3	308	33.7
$NaNO_3$	333	36.6
$AgNO_3$	250	26.9
$AgCl$	455	18.5
$AgBr$	430	14.3
$PbCl_2$	498	33.7
$PbBr_2$	488	28.6

For liquids which, for other reasons, are believed to be composed of a single molecular species, the specific heat usually rises with increasing temperature; in the case of liquid sulphur, Lewis and Randall[3] observed, however, a great rise at 160° C., which they accounted for as due to the transition from S_λ to S_μ.

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[1] *J. Am. Chem. Soc.*, **42**, 1621 (1920).

[2] *Phys. Rev.*, **28**, 1 (1909).

[3] *J. Am. Chem. Soc.*, **33**, 476 (1911).

TABLE XII

SPECIFIC HEAT OF LIQUID SULPHUR

Temp.	c_p	Temp.	c_p
100° C.	0.23	200° C.	0.27
140	0.25	300	0.27
160	0.45	400	0.28
180	0.28		

Specific Heat of Solids: The specific heat of solids at room temperature can be readily determined by heating the substance electrically in a Dewar vessel, using a bath liquid that does not react with the solid. The accuracy of this method depends on the relative heat capacities of the substance and the calorimeter.

White[1] has determined the mean specific heat of platinum and some silicates between 1500° C. and room temperature. The material was heated in an electric furnace and then dropped directly into the calorimeter. He used as great a temperature rise as 23° C. in some of his experiments.

Harper[2] gives a complete resumé of the work done on the specific heat of copper and uses a vacuum method in his experiments with the copper serving as its own calorimeter.

A large amount of work has been done on the variation of the specific heat of solids with temperature at low temperatures and Nernst[3] has given a fairly complete account of this work.

The Copper Calorimeter: The copper calorimeter was developed first by Nernst, Koref, and Lindemann.[4] It works on the principle of a mixing calorimeter with a well-insulated copper block *K* in a Dewar vessel serving as the calorimeter. Temperature changes are measured by thermoelements *I* one end of which is placed in the copper block *K*, the other in the copper cover *C*. The whole apparatus is covered with a thin copper sheeting and immersed in a constant temperature bath. The substance whose specific heat is desired is introduced at a known temperature through the tube *R* and the tempera-

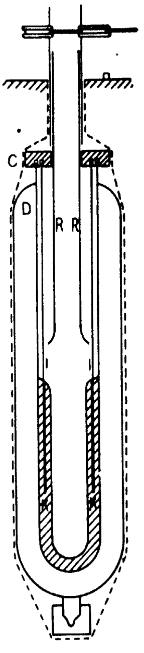

FIG. 9. Copper Calorimeter for Specific Heat

ture change determined. Koref[1] has made a number of determinations, using this method. He finds that it works quickly and accurately with a properly constructed calorimeter and that, for determining small amounts of energy, it is preferable to the ice calorimeter. Magnus[2] has used the same method for determining specific heats up to 730° C., employing a large copper block so that his percentage heat losses were smaller. The method, however, only gives average specific heats over a range of temperature.

---

[1] *Am. J. Sci.*, **28**, 334 (1909).

[2] *Bull. Bur. Standards*, **11**, 259 (1914).

[3] Grundlagen des neuen Wärmesatzes, Knapp, 1918. See also T. Estreicher, Sammlung Chem. Vortrage, **20**, 353 (1914), also, Chapter XVII.

[4] *Sitz.-ber. preuss. Akad. Wiss.*, 247 (1910).

The Vacuum Calorimeter: The principle of the vacuum calorimeter is that the substance itself serves as the calorimeter; a measured quantity of heat energy is supplied and the temperature rise measured. Several forms of this calorimeter have been developed for low temperature work.[3] In the usual form, the same wire is used for heater and resistance thermometer; at liquid hydrogen temperatures this has proved impracticable so that Schwers used a thermoelement. Gibson and Giauque[4] have used this method and modified the calorimeter slightly.

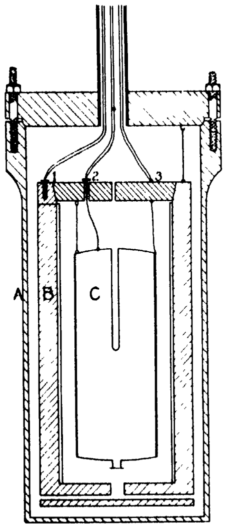

Fig. 10. Vacuum Calorimeter for Specific Heat

A diagram of the apparatus is shown in Fig. 10. The calorimeter *C* consists of a thin-walled copper vessel in which the substance to be measured is placed. It is wound with silk-covered copper wire which serves both as heater and thermometer. The whole is coated with shellac and covered with gold foil to cut down radiation corrections. The calorimeter is suspended in a massive copper cylinder *B* the inner wall of which is a thin copper cylinder on which is wound a thermometer heater of the same description as that used for the calorimeter. The leads from the calorimeter have a large insulated surface of contact with the cylinder to prevent heat leakage from outside into the calorimeter. The cylinder in turn is suspended from a vacuum-tight container *A*. The whole is placed in a Dewar vessel containing the cooling liquid; for the range 70°–150° K., liquid air is used, 160°–200° K., carbon dioxide-ether mixture and for 200°–270° K., carbon tetrachloride. The great heat capacity of the copper cylinder causes its temperature to remain practically constant even with a difference of 80° between it and the bath.

The following table for glycerol glass illustrates some of the values obtained.

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[1] *Ann. Physik*, **36**, 49 (1911).

[2] *Physik. Z.*, **14**, 5 (1913).

[3] Eucken, *Physik. Z.*, **10**, 586 (1909). Pollitzer, *Z. Elektrochem.*, **17**, 5 (1911). Nernst and Schwers, *Sitz.-ber. preuss. Akad. Wiss.*, 355 (1914).

[4] *J. Am. Chem. Soc.*, **45**, 96 (1923).

TABLE XIII

Heat Capacity of Amorphous Glycerol

Temp. ° K.	C_p per gram atom	Temp. ° K.	C_p per gram atom
70.2	0.731	192.6	2.996
93.9	0.934	227.1	3.205
122.0	1.123	275.4	3.571
153.1	1.336	299.4	3.811
179.8	1.622		

Typical data for atomic heats at various temperatures are given in Table XIV.

TABLE XIV

Atomic Heats at Low Temperatures

	° K.	C_p		° K.	C_p		° K.	C_p
Silver	35	1.58	Copper ..	33.4	0.54	Lead	23	2.96
	85	4.42		88	3.38		80	5.72
	120	5.20		120	4.58		120	5.93
	200	5.78		200	5.44		200	6.10
	280	6.01		280	5.80		280	6.28
	360	6.21		360	6.02		360	6.45

In Table XV the mean atomic heats of various silicates are given.

TABLE XV

Mean Atomic Heats of Silicates at Different Temperatures

	0°	100°	300°	400°	500°	600°	700°	800°	900°	1000°	1300°
Silica glass ..	3.33	4.05	4.95	5.17	5.35	5.48	5.58	5.68	5.75		
Quartz ..	3.37	4.1	5.1		5.9		5.46	5.58	5.66	5.72	
Anorthite .	3.74	4.39	5.22	5.43	5.58	5.69	5.82	5.95	6.94	6.14	6.82
Microcline .	3.64	4.27	5.09	5.30	5.47	5.61	5.72	5.79	5.86	5.92	

HEAT OF COMBUSTION

A great deal of work has been done on heats of combustion since this is practically the only reaction in organic chemistry which takes place smoothly and quickly without any disturbing side reactions, a necessary feature in thermochemical investigation. The combustion takes place in excess of oxygen and carbon dioxide and water are the usual end products. The heat of combustion is determined at constant volume so that to determine ΔH the quantity ΔnRT must be added to the observed value, Δn being the number of molecules produced less those consumed.

The heat of formation may be calculated from the heat of combustion by subtracting from it the sum of the heats of formation of the carbon dioxide and water resulting from the reaction. For the combustion of sucrose,

$$C_{12}H_{22}O_{11} + 12O_2 = 12CO_2 + 11H_2O; \qquad \Delta H = -1{,}350{,}000 \text{ cals.}$$

The sum of the heats of formation of the carbon dioxide and water gives $\Delta H = -1{,}875{,}300$ cals., so that, for the reaction,

$$12C + 11H_2 + 5\tfrac{1}{2}O_2 = C_{12}H_{22}O_{11}; \qquad \Delta H = -525{,}300 \text{ cals.}$$

The heat of any desired reaction can be calculated directly from the heats of combustion by subtracting the heats of combustion of the substance formed from those for the substances which disappeared. For the reaction

$$C_2H_5OH + C_6H_5COOH = C_6H_5COOC_2H_5 + H_2O,$$

we can calculate from the data in ensuing tables that $\Delta H = +1200$ cals. It is at once seen that this quantity is a difference between two very large quantities and is likely to be very greatly in error.

Some very important results have been obtained from the heats of combustion of different allotropic modifications of the elements. When the three forms of carbon are burned in oxygen, the heats absorbed are given by the following equations:

$$\begin{aligned} \text{C (diamond)} + O_2 &= CO_2; & \Delta H &= -94{,}300 \text{ cals.,}\\ \text{C (graphite)} + O_2 &= CO_2; & \Delta H &= -94{,}800 \text{ `` ,}\\ \text{C (amorphous)} + O_2 &= CO_2; & \Delta H &= -97{,}650 \text{ `` .} \end{aligned}$$

It is thus apparent that the internal energy of amorphous carbon is greatest and that for the reaction

$$\text{C (diamond)} = \text{C (graphite)}; \qquad \Delta H = +500 \text{ cals.}$$

Similarly, for other allotropic changes, the following heat effects have been observed:

$$\begin{aligned} \text{S (monoclinic)} &= \text{S (rhombic)}; & \Delta H &= -230 \text{ cals.,}\\ \text{P (white)} &= \text{P (red)}; & \Delta H &= -371 \text{ `` ,}\\ O_3 &= 1\tfrac{1}{2}O_2; & \Delta H &= -3620 \text{ `` .} \end{aligned}$$

Dickinson [1] gives the following heats of combustion as standards for calibrating combustion bombs:

Substance	$\Delta H_{20°}$
Naphthalene	$-1{,}231{,}600 \pm 250$
Benzoic acid	$-772{,}130 \pm 125$
Sucrose	$-1{,}350{,}000 \pm 700$

Richards and Davis [2] have measured the heats of combustion of several compounds with a high degree of accuracy.

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[1] *Loc. cit.*

[2] *J. Am. Chem. Soc.*, **42**, 1599 (1920).

TABLE XVI

HEATS OF COMBUSTION

Substance	ΔH
Sucrose	− 1,349,400 cals.
Benzoic acid	− 771,550
Naphthalene	− 1,231,600
Benzene	− 781,850
Toluene	− 935,230
Methyl alcohol	− 170,610
Ethyl "	− 327,040
Propyl "	− 485,800
Butyl "	− 638,330
Isobutyl "	− 637,140

The heats of combustion of the hydrogenated benzenes are characteristic of the thermal behavior of aromatic compounds.

TABLE XVII

HEATS OF COMBUSTION OF BENZENE AND HYDRO-BENZENES

Substance	ΔH	Difference
Benzene	− 779,800	68,200
Di-hydro-benzene	− 848,000	41,000
Tetra-hydro-benzene	− 982,000	41,200
Hexa-hydro-benzene	− 933,200	58,000
Hexane	− 991,200	

The transformation of benzene into its first hydrogenation product is accompanied by a much greater absorption of heat than occurs in the subsequent steps.

From an investigation of a large number of aliphatic compounds Thomsen found that, for an increase of a CH_2 group in a homologous series, there is an increase in the heat of combustion of − 157,870 cals.

TABLE XVIII

ΔH FOR SATURATED HYDROCARBONS

Substance	ΔH	Increase in ΔH for CH_2
Methane	− 310,800	− 158,200
Ethane	− 369,000	− 158,500
Propane	− 527,500	− 158,600
Tetra-methyl-methane	− 844,800	

TABLE XIX

ΔH FOR BENZENE AND DERIVATIVES[1]

Substance	Heat of Vaporization	ΔH (Liquid)	ΔH (Vapor)	Difference
Benzol	− 7450	− 780,000	− 787,400	− 155,800
Toluol	− 7990	− 935,200	− 943,200	− 154,700
Ethyl benzol	− 8140	− 1,089,800	− 1,097,900	− 155,300
n-Propyl benzol	− 8620	− 1,244,600	− 1,253,200	

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[1] Richards and Barry, *J. Am. Chem. Soc.*, **37**, 993 (1915). Richards and Davis, *ibid.*, **39**, 341 (1917).

The value of $d\Delta H$ for an additional CH_2 in an aromatic homologous series is − 155,000 cals., so that this value is approximately the same for both aliphatic and aromatic compounds.

TABLE XX

HEATS OF COMBUSTION OF ISOMERIC OCTANES[1]

Substance	Heat of Vaporization	ΔH (Liquid)	ΔH (Vapor)
n-octane	− 8120	− 1,300,500	− 1,308,600
2 methyl heptane	− 7880	− 1,301,900	− 1,309,800
2.5 dimethyl hexane	− 7650	− 1,299,200	− 1,306,900
3.4 " "	− 7880	− 1,299,700	− 1,307,600
3 ethyl hexane	− 7880	− 1,298,300	− 1,306,200
		Mean	− 1,307,800

[1] Richards and Jesse, *J. Am. Chem. Soc.*, **32**, 292 (1910).

Thomsen found from a study of the heats of combustion of the paraffins and olefines the influence of an additional carbon atom on the heat of combustion.

TABLE XXI

HEATS OF COMBUSTION OF VARIOUS ORGANIC COMPOUNDS

Compound	Formula	ΔH	Difference
Methane	CH_4	− 211,930	− 121,420
Ethylene	C_2H_4	− 333,350	
Methyl chloride	CH_3Cl	− 164,770	− 121,390
Mono chlor ethylene	C_2H_3Cl	− 286,160	
Trimethyl methane	C_4H_{10}	− 687,190	− 120,440
Isoamylene	C_5H_{10}	− 807,630	− 125,290
Diallyl	C_6H_{10}	− 932,820	

Fajans[2] has shown a possible method of calculating the energy values for the individual linkages in aliphatic hydrocarbons. From the work of the Braggs[3] on the X-ray spectrum of the diamond, we know that every C-atom is at the middle of a regular tetrahedron at whose corners are four other C-atoms and that all the linkages are similar. Thus, in the diamond, one has tetravalent carbon and the forces exerted must be similar to those between C-atoms in aliphatic compounds.

The values obtained in combustion experiments can be considered as made up of several simpler quantities: (1) the energy of a carbon hydrogen linkage C-H (x), (2) the energy of a simple C-C linkage (y), (3) the heat of formation of liquid water from 1 g-atom atomic hydrogen and molecular oxygen (v)

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[2] *Ber.*, **53**, 643 (1920).

[3] *Z. anorg. Chem.*, **90**, 227 (1915).

and (4) the heat of formation of gaseous carbon dioxide from 1 *g*-atom monatomic carbon vapor and molecular oxygen (z). For propane,

$$- 8x + 8v - 2y + 3z = - 526{,}700.$$

For ethane,

$$- 6x + 6v - y + 2z = - 370{,}000.$$

From these and similar equations a value for $z - 2y$ can be obtained, which amounts to − 98,000 ± 8000 cals. and is comparable with the heat of combustion of the diamond, − 94,400 cals. This shows that the energy of a C-C linkage in aliphatic hydrocarbons and in the diamond are approximately the same.

The value of (v) the heat of combustion of atomic hydrogen can be calculated from the dissociation of molecular hydrogen,[1] $\Delta H = 81{,}300 \pm 5700$ cals., and the heat of formation of water from hydrogen and oxygen gas, $\Delta H = - 67{,}000$ cals. Hence (v) = − 74,400 ± 2800 cals.

Fajans[2] has discussed the methods for obtaining the heat of sublimation of carbon and has accepted a value of + 287,000 cals. Two methods have been used for calculating this quantity: one due to Gruneisen,[3] based on a relationship between specific heat and thermal expansion, and the other due to Lummer[4] who measured the effect of pressure on the temperature of the positive crater of a carbon arc. There is some uncertainty in this value as it differs greatly from that calculated from the Nernst Heat Theorem.

From the value z, the heat of combustion of monatomic carbon vapor is − 381,000 cals.

The following table gives the heat of formation of some simple aliphatic hydrocarbons.

TABLE XXII

HEATS OF FORMATION OF ALIPHATIC HYDROCARBONS

Substance	Heat of Combustion	Heat of Formation from Diamond + H_2	Heat of Formation from Atoms	ΔH for CH_2
Methane	− 211,000	− 18,000	− 468,000	− 370,000
Ethane	− 370,000	− 21,000	− 838,000	− 373,000
Propane	− 527,000	− 26,000	− 1,211,000	
Ethylene	− 340,000	16,000	− 720,000	− 375,000
Propylene	− 494,000	8,000	− 1,095,000	
Acetylene	− 312,000	56,000	− 599,000	− 370,000
Allylene	− 472,000	54,000	− 969,000	

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[1] Langmuir, *Z. Elektrochem.*, **23**, 417 (1917). Isnardi, *ibid.*, **21**, 417 (1915). Franck, Knipping and Kruger, *Verh. D. physik. Ges.*, **21**, 729 (1919).

[2] *Z. Physik.*, **1**, 101 (1920).

[3] *Verh. D. physik. Ges.*, **14**, 324 (1912).

[4] *Verflussigung der Kohle*, 1914. Sammlung Vieweg.

From this table, it is seen that the increase of a C-atom and 2 H-atoms to form a CH_2 group in different compounds is accompanied by an approximately constant increase in heat content. For the $C = C$ linkage, $\Delta H = -252{,}000$ cals., and, for the $C \equiv C$ linkage, $\Delta H = -365{,}000$ cals.

Considering the two oxides of carbon as formed from atomic carbon and oxygen,

$$C \text{ (vapor)} + \tfrac{1}{2}O_2 = CO; \qquad \Delta H = -314{,}000 \text{ cals.}$$
$$CO + \tfrac{1}{2}O_2 = CO_2; \qquad \Delta H = -\ \ 67{,}000 \text{ cals.}$$

Hence, the energy change accompanying the combination with the first oxygen atom is much greater than with the second.

HEAT OF SOLUTION

By *heat of solution* one understands the amount of heat that is absorbed when one mol. of a substance is dissolved in so large a volume of solvent that further dilution causes no further absorption of heat. The heat absorbed when 1 mol. of a substance is dissolved in a solvent to form a given solution is called the *total heat of solution*. If, however, a small amount of solute is added to a given solution, the heat evolved per mol. is called the *partial heat of solution* for that particular concentration. These two quantities are identical in very dilute solutions, but, for concentrated solutions, they may be very different from one another.

In thermodynamic calculations the partial heats of solution are the quantities employed and the accompanying illustration will show how these quantities may be derived from the total heats of solution which are the quantities usually found in the literature.

Brönsted[1] has measured the heats of formation of sulphuric acid solutions from H_2SO_4 and H_2O and gives the following values.

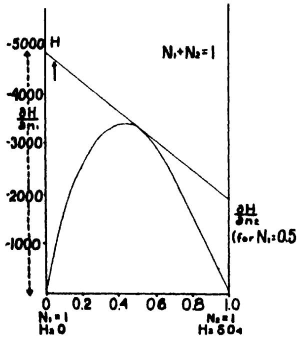

FIG. 11. Heat of Solution of H_2SO_4

The third column gives the heat absorbed per mol. of solution formed. In Fig. 11 the heat of formation per mol. of solution from acid and water is plotted as ordinate against the mol. fraction of acid as abscissa. A tangent to the curve is drawn at $N_2 = 0.50$; the intercepts of this tangent on the ordinates $N_1 = 1$ and $N_2 = 1$ are equal respectively to $\overline{H}_1$ and $\overline{H}_2$, where

$$\overline{H}_1 = \frac{\partial H}{\partial n_1} \quad \text{and} \quad \overline{H}_2 = \frac{\partial H}{\partial n_2},$$

where n_1 and n_2 are the number of mols. of water and acid in any given amount of solution. To prove this relationship,

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[1] *Z. physik. Chem.*, 68, 700 (1909).

TABLE XXIII

HEATS OF SOLUTION OF SULPHURIC ACID AND WATER

Mol. Fraction Acid—N_2	Heat Evolved per Mol. Acid	ΔH per Mol. Soln.	Mol. Fraction Acid N_2	Heat Evolved per Mol. Acid	ΔH per Mol. Soln.
0.00008	20,430	− 1.6	0.10	15,610	− 1561
0.00016	20,150	− 3.2	0.15	14,170	− 2125
0.00024	19,900	− 4.78	0.20	12,940	− 2588
0.00032	19,660	− 6.14	0.25	11,880	− 2969
0.00040	19,400	− 7.76	0.30	10,710	− 3213
0.000625	18,990	− 11.87	0.35	9,650	− 3378
0.00125	18,540	− 23.2	0.40	8,630	− 3452
0.00250	18,100	− 45.2	0.45	7,680	− 3456
0.0050	17,760	− 88.8	0.50	6,730	− 3365
0.01	17,600	− 176	0.55	5,810	− 3195
0.02	17,360	− 347.2	0.60	4,870	− 2932
0.03	17,200	− 516	0.65	4,060	− 2639
0.04	17,060	− 682.4	0.70	3,280	− 2296
0.05	16,900	− 845	0.75	2,600	− 1950
0.06	16,710	− 1002.6	0.80	1,970	− 1576
0.07	16,460	− 1152.2	0.85	1,420	− 1207
0.08	16,200	− 1296	0.90	930	− 837
0.09	15,910	− 1431.9	0.95	150	− 427

it is necessary to show that

$$H - N_2\frac{dH}{dN_2} = \frac{\partial H}{\partial n_1}, \tag{33}$$

where the mol. fraction of acid N_2 is equal to $\frac{n_2}{n_1 + n_2}$. Since

$$H = \frac{\boldsymbol{H}}{n_1 + n_2}, \tag{34}$$

where $\boldsymbol{H}$ is the heat content of a solution containing n_1 mols. of water and n_2 mols. of acid,

$$dH = \frac{d\boldsymbol{H}}{n_1 + n_2} - \frac{dn_1}{(n_1 + n_2)^2} \tag{35}$$

and $dN_2 = -\frac{n_2 dn_1}{(n_1 + n_2)^2}$, if we assume n_2 constant and vary N_2 by varying n_1. Then

$$N_2\frac{dH}{dN_2} = -\frac{dH}{dn_1} + \frac{\boldsymbol{H}}{n_1 + n_2} = -\frac{\partial H}{\partial n_1} + H. \tag{36}$$

Substituting this in the original equation the result follows. It can also be shown that

$$\boldsymbol{H} = n_1\frac{\partial H}{\partial n_1} + n_2\frac{\partial H}{\partial n_2} \tag{37}$$

and

$$\frac{dH}{dN_1} = -\frac{dH}{dN_2} = \frac{\partial H}{\partial n_1} - \frac{\partial H}{\partial n_2}. \tag{38}$$

The quantity $\frac{\partial H}{\partial n_1}$ is the partial heat of solution of water in the acid solution of mol. fraction N_2 or the partial molal heat content of the water in the solution. Hence the intercept of the tangent on the ordinate $N_2 = 1$ gives the partial heat of solution of 1 mol. of acid in a large quantity of solution of mol. fraction $N_2 = 0.50$.

In a very similar manner the heat effect when one mol. of solution of composition $N_2 = 0.20$ is added to a large quantity of composition $N_2 = 0.50$ can be determined. The intercept of the ordinate at $N_2 = 0.20$ between the curve and the tangent to the curve at $N_2 = 0.50$ gives the measure of this heat effect. This can be shown as follows:

0.2 mol. acid + l.q. soln. ($N_2 = 0.50$); $\Delta H = 0.2\bar{H}_2\ (N_2 = 0.50)$,
0.8 mol. water + l.q. soln. ($N_2 = 0.50$); $\Delta H = 0.8\bar{H}_1\ (N_2 = 0.50)$,
0.2 mol. acid + 0.8 mol. water; $\Delta H = H\ (N_2 = 0.20)$,
1 mol. soln. ($N_2 = 0.20$) + l.q. soln. ($N_2 = 0.50$); $\Delta H = ?$,
$? = 0.2\bar{H}_2\ (N_2 = 0.50) + 0.8\bar{H}_1\ (N_2 = 0.50) - H\ (N_2 = 0.20)$.

This corresponds to the intercept mentioned above. In general when 1 mol. of solution of composition x_1 is mixed with a large quantity of solution of composition x_2, the heat effect is calculated by drawing a tangent to the curve at x_2 and determining the distance from where this cuts the ordinate x_1 to the curve.

If one mol. of solution of composition $N_2 = 0.20$ is mixed with three mols. of composition $N_2 = 0.60$, the heat effect can be determined in a similar manner.

0.2 mol. acid + 0.8 mol. water, $\Delta H = H\ (N_2 = 0.20)$,
3 × 0.6 mol. acid + 3 × 0.4 mol. water; $\Delta H = 3H\ (N_2 = 0.60)$,
2 mol. acid + 2 mol. water; $\Delta H = 4H\ (N_2 = 0.50)$,
1 mol. soln. ($N_2 = 0.20$) + 3 mol. soln.; ($N_2 = 0.60$) $\Delta H = ?$,
$? = 4H\ (N_2 = 0.50) - H\ (N_2 = 0.20) - 3H\ (N_2 = 0.60)$.

In the diagram the chord joining the points on the curve corresponding to $N_2 = 0.50$ and $N_2 = 0.60$ is produced to cut the ordinate at $N_2 = 0.20$ and the distance between this point and the curve gives the heat effect.

Relative Nature of Values for Heat Content Used: H is the molal heat content of the solution when the molal heat contents of the pure acid and water are assumed to be zero and similarly $\bar{H}_1$ and $\bar{H}_2$ are the partial molal heat contents of the water and acid in the solution referred to the heat content of the pure substances as zero.

Of course it is not necessary to make these particular assumptions concerning the position of the zero point on the diagram. We might have considered the heat content of the system $SO_3 + H_2O$ as zero when $N_2 = 1$, in which case the zero or base line of the curve would be displaced to 20,400 on the ordinate $N_2 = 1$ on the present diagram. The base line might even have been considered as drawn between the points giving the heat contents of the elements from which the water and acid are formed. Lewis and Randall[1] use as their base line the heat contents of the substances in infinitely dilute solutions. Fig. 12 shows the positions of these various base lines with reference to the curve. It will be seen from the above discussion that the absolute values assigned to the various points is of no importance since we are dealing solely with ΔH which is the difference between two H's. The particular values assigned to the various points have no physical significance since we are unable to determine absolute values for the heat content of any substance.

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[1] Thermodynamics. McGraw-Hill Co., page 88.

Calculation of Partial Molal Heat Content for the Solvent when that for Solute is Known: We know that

$$H = n_1 \frac{\partial H}{\partial n_1} + n_2 \frac{\partial H}{\partial n_2}$$

and, since

$$dH = \frac{\partial H}{\partial n_1} dn_1 + \frac{\partial H}{\partial n_2} dn_2, \qquad (39)$$

it can be seen that

$$n_1 d\left(\frac{\partial H}{\partial n_1}\right) + n_2 d\left(\frac{\partial H}{\partial n_2}\right) = 0. \qquad (40)$$

So

$$\int d\left(\frac{\partial H}{\partial n_1}\right) = -\int \frac{N_2}{N_1} d\left(\frac{\partial H}{\partial n_2}\right). \qquad (41)$$

If, now, the values of $\frac{\partial H}{\partial n_2}$ are given, it is possible to determine those for $\frac{\partial H}{\partial n_1}$ if the value is known for $\frac{\partial H}{\partial n_1}$ when $\frac{\partial H}{\partial n_2} = 0$. To do this, the values of $\frac{N_2}{N_1}$ are plotted as ordinates against $\frac{\partial H}{\partial n_2}$ as abscissæ. The negative value of the area under the curve between $N_1 = 0$ and $N_1 = N_1'$ gives the difference between the values of $\frac{\partial H}{\partial n_1}$ for $N_1 = N_1'$ and $N_1 = 0$. To determine a series of values of $\frac{\partial H}{\partial n_1}$, it is necessary to know from experiment the limiting value of $\frac{\partial H}{\partial n_1}$ as N_1 approaches zero.

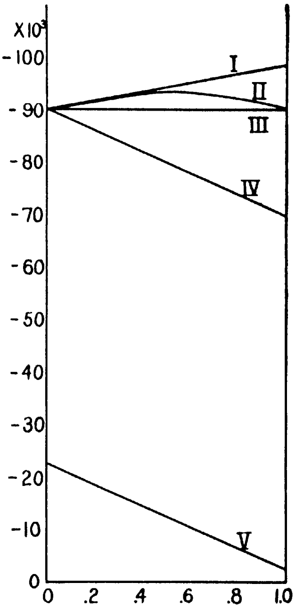

FIG. 12 Heat Content of Sulphuric Acid Solutions Referred to Varying Initial States

I. Lewis and Randall reference state

II. Curve for solution

III. Heat content water and acid reference state

IV. Heat content sulfur trioxide and water reference state

V. Heat content elements reference state

Bronsted gives a series of values for $\frac{\partial H}{\partial n_2}$ for sulphuric acid solutions of varying strengths and these are given in Table XXIV. These results are plotted in Fig. 13 and the values for the area determined by counting squares.

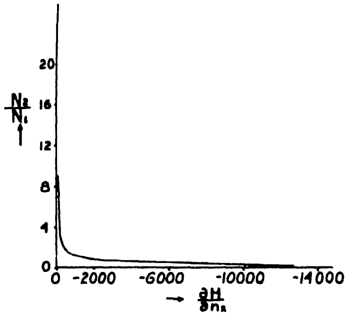

FIG. 13. Partial Molal Heat Content of Sulphuric Acid in Aqueous Solutions

TABLE XXIV

PARTIAL MOLAL HEAT CONTENT OF SULPHURIC ACID SOLUTIONS

Mol. Fraction Acid—N_2	$\frac{N_2}{N_1}$	$\frac{\partial H}{\partial n_2}$	Mol. Fraction Acid—N_2	$\frac{N_2}{N_1}$	$\frac{\partial H}{\partial n_2}$
0.0001	.0001	− 20,050	0.45	.818	− 2960
0.01	.0101	− 17,250	0.50	1.00	− 1890
0.05	.0526	− 16,070	0.55	1.22	− 1160
0.08	.0870	− 14,260	0.60	1.5	− 670
0.10	.111	− 12,970	0.65	1.86	− 460
0.15	.175	− 10,890	0.70	2.33	− 290
0.20	.250	− 9,010	0.75	3.00	− 173
0.25	.333	− 7,520	0.80	4.00	− 102
0.30	.429	− 6,230	0.85	5.67	− 64
0.35	.539	− 5,070	0.90	9.00	− 47
0.40	.666	− 4,040	0.95	19.00	− 28

Table XXV gives the values obtained between the different concentrations. Column 2 gives differential values for $\frac{\partial H}{\partial n_1}$ between concentrations that differ by 0.05 from one another. Column 3 gives values for $\frac{\partial H}{\partial n_1}$ at varying values for N_2, assuming a value of − 8350 cals. for $\frac{\partial H}{\partial n_1}$ when $N_1 = 0$. Column 4 gives similar values calculated by Bronsted and Column 5 values determined experimentally by Rumelin.[1]

TABLE XXV

HEAT CONTENT DATA FOR SULPHURIC ACID SOLUTIONS

Mol. Fraction Acid—N_2	Differential Values $\frac{\partial H}{\partial n_1}$	$\frac{\partial H}{\partial n_1}$ (calc.)	$\frac{\partial H}{\partial n_1}$ (Bronsted)	$\frac{\partial H}{\partial n_1}$ (Rumelin)
0.95	266	− 8161		
.90	124	− 7895		
.85	184	− 7771		
.80	248	− 7587		
.75	339	− 7339		
.70	364	− 7000		
.65	353	− 6636		
.60	617	− 6283		
.55	811	− 5666		
.50	973	− 4855	− 4850	
.45	801	− 3882	− 3880	
.40	620	− 3081	− 3060	
.35	560	− 2461	− 2470	
.30	490	− 1901	− 1910	− 1810
.25	434	− 1410	− 1450	− 1415
.20	399	− 976	− 1000	− 985
.15	297	− 577	− 580	− 630
.10		− 280	− 280	− 275

In the following table some values for heats of dilution are given for nitric, hydrochloric and oxalic acids.

TABLE XXVI

HEATS OF DILUTION

Mols. Water per 1 Mol. Acid	HNO_3	HCl	$C_2H_2O_2$
1	− 3340	− 5,370	+ 152
2	− 4860	− 11,360	+ 156
5	− 6760	− 14,960	
8	− 7220		
10	− 7270	− 16,160	
20	− 7360	− 16,760	− 173
50		− 17,100	− 278
100	− 7210	− 17,200	− 335
200	− 7180		− 375
300		− 17,300	

---

[1] *Z. physik. Chem.*, **58**, 449 (1907).

For gases, the heat of solution ΔH is negative, which is also true, as a rule, for liquids; for solids, it may be either positive or negative. The explanation of this is simple: if one assumes that ΔH is always negative for a gas, then the sign of ΔH for a liquid depends on whether the heat of vaporization is greater than the heat of solution and for the solid state on the difference between the heat of sublimation and of solution of the corresponding gas.

Thomsen[1] pointed out that, as a rule, the heat of solution of difficultly soluble substances of similar chemical properties is greater the more insoluble the substance is.

The heat of precipitation is the negative value of the heat of solution. Table XXVII gives values for the integral heat of solution of a number of metallic compounds.

TABLE XXVII

INTEGRAL HEATS OF SOLUTION FOR METALLIC COMPOUNDS

Substance	Mols. H_2O per Mol. Salt	ΔH
$LiOH$	400	− 5,800
$NaOH$	200	− 9,900
KOH	250	− 13,300
$BaCl_2$	400	2,100
$BaCl_22H_2O$	400	4,900
$FeCl_2$	350	− 17,900
$FeCl_24H_2O$	400	− 2,750
$CaBr_2$	400	− 24,510
$CaBr_26H_2O$	400	1,100
$ZnSO_4$	400	− 18,400
$ZnSO_47H_2O$	400	4,260
$Ca(NO_3)_2$	400	− 3,950
$Ca(NO_3)_24H_2O$	400	7,250
$CaSO_4$	∞	− 4 400
$CaSO_42H_2O$	∞	300
CaI_2	400	− 27,700

Comparing the heats of solution with one another, it is seen that anhydrous salts which can be in equilibrium with their saturated solutions at room temperature usually dissolve with an absorption of heat while anhydrous salts which form hydrates at room temperature generally dissolve with evolution of heat since their heats of hydration are generally very large.

Thermochemistry of Electrolytes: When one mixes two dilute salt solutions and a precipitate is not formed, there is usually no heat effect. This is the so-called Law of Thermoneutrality of Salt Solutions. There are a few exceptions to this rule where an unionized salt is produced by the reaction

$$2KCl\,aq + Hg(NO_3)_2\,aq = 2KNO_3\,aq + HgCl_2\,aq; \quad \Delta H = -12{,}400 \text{ cals.}$$

The difference between the heat of formation of two salt solutions having a common ion depends on the nature of the two other ions and is independent of the common ion.

---

[1] *J. prakt. Chem.*, (2) 13, 241 (1876).

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 + aq = HCl\ aq; \qquad \Delta H = -\ 39{,}320,$$
$$\tfrac{1}{2}H_2 + \tfrac{1}{2}I_2 + aq = HI\ aq; \qquad \Delta H = -\ 13{,}170,$$
$$\tfrac{1}{2}Cl_2 + HI\ aq = \tfrac{1}{2}I_2 + HCl\ aq; \qquad \Delta H = -\ 26{,}150.$$

$$K + \tfrac{1}{2}Cl_2 + aq = KCl\ aq; \qquad \Delta H = -\ 101{,}170,$$
$$K + \tfrac{1}{2}I_2 + aq = KI\ aq; \qquad \Delta H = -\ 75{,}020,$$
$$\tfrac{1}{2}Cl_2 + KI\ aq = \tfrac{1}{2}I_2 + KCl\ aq; \qquad \Delta H = -\ 26{,}150.$$

When the iodide ion is replaced by chlorine in a dilute aqueous solution forming iodine, one always observes the same heat absorption. This does not hold for the replacement of the iodine in KIO_3 by chlorine since this is not an ionic reaction.

The *heat of neutralization* of a strong acid by a strong base has approximately a constant value independent of the acid or base used, as is seen from a glance at Table XXVIII.[1]

TABLE XXVIII

HEATS OF NEUTRALIZATION

Acid and Base	$\Delta H_{293°}$
KOH aq + HCl aq	− 13,695
NaOH aq + HCl aq	− 13,700
LiOH aq + HCl aq	− 13,660
KOH aq + HNO_3 aq	− 13,705
NaOH aq + HNO_3 aq	− 13,685
LiOH aq + HNO_3 aq	− 13,715

The explanation of this striking regularity follows at once from the theory of electrolytic dissociation. According to this theory, the only reaction taking place is due to the combination of the hydrogen ion of the acid with the hydroxyl ion of the base.

$$H^+ + OH^- = H_2O; \qquad \Delta H_{293°} = -\ 13{,}700\ \text{cals.}$$

If the acid or base is only partially dissociated, the heat effect accompanying its neutralization with a completely dissociated base or acid corresponds to the heat of neutralization plus the heat of dissociation of the acid or base used. In the following table are given values for the heat of neutralization of weak acids with sodium hydroxide.

TABLE XXIX

HEATS OF NEUTRALIZATION OF WEAK ACIDS WITH SODIUM HYDROXIDE

Acid	Heat Absorbed	Heat of Dissociation
Acetic	− 13,400	− 300
Dichloracetic	− 14,830	1130
Phosphoric	− 14,830	1130
Hydrofluoric	− 16,270	2570

---

[1] Richards and Rowe, *J. Am. Chem. Soc.*, **44**, 684 (1922).

If a dilute solution of the salt of a weak acid and a strong base is mixed with a strong acid, the weak acid is set free and a heat effect is observed comparable to the heat of dissociation of the weak acid.

Thomsen mixed sodium fluoride and hydrochloric acid and measured the heat absorbed by the reaction

$$\text{NaF aq} + \text{HCl aq} = \text{NaCl aq} + \text{HF aq}; \qquad \Delta H = -2360 \text{ cals.}$$

This value is not very different from that given in the preceding table.

When a formula weight of a di- or polybasic acid is neutralized in steps, the heat effects for the successive stages are generally different. When phosphoric acid is treated with sodium hydroxide at 18° C., the following values are found:

$$\begin{aligned} &H_3PO_4 + NaOH; && \Delta H = -14{,}800, \\ &NaH_2PO_4 + NaOH; && \Delta H = -13{,}600, \\ &Na_2HPO_4 + NaOH; && \Delta H = -500. \end{aligned}$$

Heats of Adsorption and Wetting

Since the amount of adsorption increases rapidly with decreasing temperature, it follows from the van't Hoff-Le Chatelier law that adsorption must be accompanied by a considerable evolution of heat. Favre,[1] Chappuis,[2] Mond, Ramsay and Shields,[3] Dewar,[4] Titoff,[5] Lamb and Coolidge,[6] and Beebe and Taylor[7] have carried out quantitative investigations on heats of adsorption of gases on solids, mostly starting with the solid in an evacuated vessel and admitting the gas to atmospheric pressure. These measurements of the integral or total heat of adsorption are comparable to a heat of solution. The differential heats of adsorption obtained over small pressure ranges are more suitable to theoretical treatment and can be likened to a heat of dilution.

In the case where the weight of adsorbed substance is held constant, with varying temperature and pressure, the heat of adsorption (isosteric) corresponds to a heat of vaporization and can be calculated from the Clapeyron-Clausius equation. For a certain value of $\frac{x}{m}$ (weight of adsorbed substance per unit weight of adsorbent) there is an equilibrium pressure p. At a temperature $dT°$ higher, for the same value of $\frac{x}{m}$, the pressure has increased to $p + dp$. The value for the heat of adsorption is given by the equation

$$\Delta H = -RT^2 \frac{dlnp}{dT}. \tag{42}$$

---

[1] *Ann. Chim. Phys.*, (5) **1**, 209 (1871).
[2] *Wied. Ann.*, **19**, 21 (1883).
[3] *Z. physik. Chem.*, **25**, 657 (1898).
[4] *Proc. Roy. Soc.*, **74**, 122 (1904).
[5] *Z. physik. Chem.*, **74**, 641 (1910).
[6] *J. Am. Chem. Soc.*, **42**, 1146 (1920).
[7] *J. Am. Chem. Soc.*, **46**, 43 (1923).

Now,

$$\frac{dlnp}{dT} = \frac{n}{\log e}(\zeta - \xi \log p), \qquad (43)^{1}$$

where the temperature coefficients of the equation for the adsorption isotherm

$$\frac{x}{m} = \alpha p^{1/n} \qquad (44)$$

are given by the equations

$$\zeta = -\frac{d \log \alpha}{dT} \qquad (45)$$

and

$$\xi = \frac{d\frac{1}{n}}{dT}. \qquad (46)$$

Hence,

$$\Delta H = -RT^2(\zeta - \xi \log p), \qquad (47)$$

where p is expressed in cm. of mercury. This equation has been tested by Titoff. He evaluated ζ and ξ through measurements of adsorption isotherms at different temperatures on coconut charcoal and determined the heat of adsorption, using an ice calorimeter. Table XXX shows the agreement between the calculated and observed values. For Titoff's calculations $\frac{x}{m}$ is not constant, but the change in it is much smaller than in p and one can make a calculation employing a mean value of p.

TABLE XXX

Heats of Adsorption on Charcoal

Gas	ζ	ξ	ΔH (calc.)	ΔH (obs.)
Nitrogen . .	0.01367	0.00297	− 3875	− 4548
Carbon dioxide	0.01420	0.00477	− 6483	− 6514
Ammonia	0.02168	0.00987	− 7764	− 7928

The following table is due to Chappuis.

[1] Freundlich, Kapillarchemie, 1922, page 161.

TABLE XXXI

HEATS OF ADSORPTION ON CHARCOAL

Gas	$\frac{r}{m}$ Before	$\frac{x}{m}$ After	p in Cm. Before	p in Cm. After	ΔH	Heat of Liquefaction
Air	0	7.44	0	70.47	– 2,400	
CO_2	22.6	44.1	8.22	36.32	– 7,300	– 6250
NH_3	105	131	12.25	22.25	– 8,100	– 5000
SO_2	70	90.6	7.06	45.1	– 10,900	– 5600
$CHCl_3$	62.2	72.3	17.48	67.54	– 10,700	

Variation of Heat of Adsorption with Pressure: As could be predicted from equation (47), the heat of adsorption decreases with increasing pressure.

TABLE XXXII

ADSORPTION OF AMMONIA ON MEERSCHAUM AT 0° C.

p in Cm.		$\frac{x}{m}$ Before	$\frac{x}{m}$ After	ΔH
Before	After			
0	0	0	24.2	– 20,500
0	0.5	24.2	48.3	– 12,700
0.5	3.71	48.3	72.3	– 11,300
2.93	21.50	72.3	95.3	– 8,970
21.50	57.56	95.3	117	– 7,600

For adsorption of gases on indifferent substances, the reaction concerned appears to be of a purely physical nature and the heat effect observed corresponds to the heat of vaporization and a heat of compression. It will be seen from Table XXXI that the heat of adsorption is greater than the heat of liquefaction.

Dewar working at – 185° C. measured the integral heat of adsorption of several gases on charcoal.

TABLE XXXIII

HEATS OF ADSORPTION ON CHARCOAL AT – 185° C.

Gas	ΔH	Heat of Liquefaction
H_2	– 1600	– 230
N_2	– 3686	– 1372
Ar	– 3636	
O_2	– 3744	– 1664
CO	– 3416	

Lamb and Coolidge, measuring the heats of adsorption for some organic vapors on charcoal, find a relation $h = mx^n$, where h is the heat evolved per gram of gas-free charcoal, x the number of cc. of gas adsorbed per gram of charcoal, and m and n constants for the vapor considered; n is found to be nearly unity, so that there is an almost linear relationship between heat of adsorption and amount adsorbed. Assuming this to correspond to a heat of compression, they calculate a pressure of 37,000 atmospheres when 1 cc. of liquid is adsorbed by 10 grams of charcoal.

Mond, Ramsay and Shields[1] have measured the heat of adsorption of oxygen on platinum black and obtained a value of $\Delta H = -17{,}600$ cals. as compared with $\Delta H = -17{,}700$ cals. determined by Thomsen for the reaction

$$Pt + \tfrac{1}{2}O_2 + H_2O = Pt(OH)_2.$$

Beebe and Taylor determined the heat of adsorption for hydrogen on finely divided nickel and obtained values ranging from $\Delta H = -14{,}300$ cals. per mol. to $\Delta H = -20{,}600$, the larger value being for the poorer adsorbent. The differential heats of adsorption for hydrogen on nickel are constant for the pressure range 0–760 mm., pointing apparently to a specific chemical action. A similar value to the above is obtained from the adsorption isosteres for hydrogen on nickel.[2]

TABLE XXXIV

ADSORPTION ISOSTERES FOR HYDROGEN ON NICKEL

Cc. H_2 Adsorbed	p		$\frac{p_1}{p_2}$
	218°	184°	
6.7	88 mm.	17 mm.	5.18
6.9	128 "	24 "	5.33
6.1	34 "	6 "	5.66
			Av.... 5.4

Integrating the Clapeyron-Clausius equation, we obtain

$$\Delta H = 1.99 \times 2.303 \times \frac{T_1T_2}{T_1 - T_2} \times \log \frac{p_2}{p_1}. \tag{48}$$

Inserting the above values, we obtain

$$\Delta H = -22{,}100 \text{ cals.}$$

Heat of Wetting: The heat of wetting is the heat absorbed when a solid surface and a liquid surface are brought together. It is the same quantity as the integral heat of adsorption of a vapor at its saturation pressure. Parks[3] has shown that the amount of heat absorbed is proportional to the surface.

---

[1] *Z. physik. Chem.*, **25**, 657 (1898).

[2] Gauger and Taylor, *J. Am. Chem. Soc.*, **45**, 920 (1923).

[3] *Phil. Mag.*, (6) **4**, 240 (1902).

Schwalbe[1] has shown that the heat of wetting of hydrated silica is negative above 4° C. and positive below that temperature. These experiments support the idea that there is a distinct connection between adsorption and compressibility. Gaudechon[2] obtained the data in Table XXXV for different adsorbents and liquids. The powders were dried at 100° C.

TABLE XXXV

HEAT OF WETTING FOR 1 G. ADSORBENT IN GRAM CALORIES

Liquid	Adsorbent		Sugar Char
	Alumina	Quartz	
Water.	− 12.6	− 15.3	− 3.9
Methyl alcohol	− 11.0	− 15.3	− 11.5
Ethyl "	− 10.8	− 14.7	− 6.9
Propyl "	− 10.2	− 13.5	− 5.6
Amyl "	− 10.1	− 13.5	− 3.7
Formic acid	− 12	− 14.5	− 12
Acetic " . . .	− 9.3	− 13.5	− 6.0
Acetone	− 8	− 13.5	− 3.6
Carbon tetrachloride . .	− 1.8	− 8.1	− 1.5

The action of water vapor on dried cotton wool[3] is very interesting. If the bulb of a thermometer be covered with carefully dried cotton wool and then dipped in water at the same temperature, the thermometer will rise 8°–12°.

HEAT OF COAGULATION OF COLLOIDS

The heat of coagulation of colloids or its converse, the heat of peptization, is the heat change involved in the subdivision of a solid to particles of colloidal size. If colloidal solutions are analogous to true solutions, this heat effect should be analogous to a heat of solution. Kruyt and van der Spek[4] found no measurable change accompanying the coagulation of arsenious sulfide hydrosol. Browne and Matthews[5] have measured the heat of coagulation of ferric oxide hydrosol of varying purity with different electrolytes. The heat effects observed are attributed to the action of the electrolyte in the coagulant upon the electrolytes, particularly ferric chloride present in the sol. With very pure sols the heat change is practically negligible: 1–2 cals. per gram equivalent of ferric oxide; one can say that for ferric oxide also there is no heat of peptization.

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[1] *Drud. Ann.*, **16**, 32 (1905).

[2] *Compt. rend.*, **157**, 209 (1913).

[3] Masson, *Proc. Roy. Soc.*, **74**, 230 (1904).

[4] *Kolloid Z.*, **24**, 145 (1919).

[5] *J. Am. Chem. Soc.*, **43**, 2336 (1921); **45**, 311 (1923).

HEAT OF HYDRATION OF GAS IONS

Born[1] has introduced a new thermochemical magnitude which he terms the *lattice energy* of crystals and which is defined as the energy necessary for the formation of free gaseous ions from crystals. He has calculated this magnitude for a number of crystals from a knowledge of their molecular volume. Fajans[2] has shown that this complex effect may be considered as the sum of a number of simpler reactions. Introducing a new magnitude, the *heat of hydration of gas ions,* he shows that the heat of solution of a salt is the difference between the heat necessary for the dissociation of the crystal into free gas ions, i.e., the lattice energy, and the heat of solutions of these same ions in water. It is this latter quantity which is designated as the heat of hydration of the gas ions. According to Fajans, one is to assume that in the solution of the gas ion the oppositely charged parts of the polar water molecules in its neighborhood are oriented towards the ion and they in turn act upon molecules farther away.

$$\begin{array}{ll} K^+(g) + Cl^-(g) & = KCl(s) + U \\ KCl(s) + aq & = K^+aq + Cl^-aq + L \\ \hline K^+(g) + Cl^-(g) + aq & = K^+aq + Cl^-aq + (U + L) \end{array}$$

where U is obtained from lattice energy data, L is the heat of solution and $(U + L) = W$, where W is the heat of hydration of the gas ions. Fajans gives the following table of values for W for a number of alkali halides.

TABLE XXXVI

Salt	W_{salt}	Salt	W_{salt}	Salt	W_{salt}
LiCl	– 187,000	LiBr	– 178,000	LiI . .	– 168,000
NaCl..	– 180,500	NaBr	– 171,000	NaI .	– 159,000
KCl . .	– 159,000	KBr	– 150,000	KI ..	– 139,000
RbCl	– 150,000				
CsCl.........	– 151,000				
TlCl.... ...	– 159,000				

The values of W for the salts are purely additive quantities, depending on the values for the individual gas ions, so that, if differences are taken for a series of salts for two metals with common cations, the same values should be obtained. Table XXXVII illustrates this.

TABLE XXXVII

	Cl	Br	I
$W_{Li^+} - W_{K^+}$	– 28,000	– 28,000	– 29,000
$W_{Na^+} - W_{K^+}$	– 21,500	– 21,000	– 20,000

---

[1] *Ber. deut. physik. Ges.*, **21**, 13 (1919).

[2] *Ber. deut. physik. Ges.*, **21**, 549, 714 (1919).

Fajans[1] has developed another method for determining the differences between the heats of hydration of two gas anions independent of the lattice energy concept. The method employed is illustrated by the following process:

$$
\begin{array}{lll}
\mathrm{K}\,(s) + \mathrm{aq} = \mathrm{K}^+\,\mathrm{aq} + \mathrm{OH}^-\,\mathrm{aq} + \tfrac{1}{2}\mathrm{H}_2\,(g); & \Delta H = -\ 48{,}100, & (a) \\
\mathrm{H}^+\,\mathrm{aq} + \mathrm{OH}^-\,\mathrm{aq} = \mathrm{aq}; & \Delta H = -\ 13{,}600, & (b) \\
\mathrm{K}\,(s) + \mathrm{H}^+\,\mathrm{aq} + \tfrac{1}{2}\mathrm{H}_2\,(g); & \Delta H = -\ 61{,}700, & (c) \\
\mathrm{K}\,(g) = \mathrm{K}\,(s); & \Delta H = -\ 21{,}000, & (d) \\
\mathrm{K}^+\,(g) + \ominus = \mathrm{K}\,(g); & \Delta H = -\ 99{,}000, & (e) \\
\tfrac{1}{2}\mathrm{H}_2\,(g) = \mathrm{H}\,(g); & \Delta H = +\ 45{,}000, & (f) \\
\mathrm{H}\,(g) = \mathrm{H}^+\,(g) + \ominus; & \Delta H = \ \ 312{,}000, & (g)
\end{array}
$$

whence

$$
\mathrm{K}^+\,(g) + \mathrm{H}^+\,\mathrm{aq} = \mathrm{H}^+\,(g) + \mathrm{K}^+\,\mathrm{aq}; \qquad \Delta H = \ 175{,}000, \qquad (h)
$$

and since

$$
\begin{array}{lll}
\mathrm{H}^+\,(g) + \mathrm{aq} = \mathrm{H}^+\,\mathrm{aq}; & \Delta H = W_{\mathrm{H}^+}, & (i) \\
\mathrm{K}^+\,(g) + \mathrm{aq} = \mathrm{K}^+\,\mathrm{aq}; & \Delta H = W_{\mathrm{K}^+}, & (j)
\end{array}
$$

equation (*h*) gives us

$$
W_{\mathrm{H}^+} - W_{\mathrm{K}^+} = -\ 175{,}000 \text{ cals}
$$

Equations (*a*) and (*b*) give the heat effect of two reactions that take place in solutions, (*d*) gives the heat of sublimation of potassium, (*f*) the heat of dissociation of hydrogen, (*e*) the heat effect corresponding to the ionization potential of potassium and (*g*) that corresponding to the ionization potential of atomic hydrogen. Other reactions have been worked out in an analogous manner and the following values obtained:

$$
\begin{array}{l}
W_{\mathrm{Na}^+} - W_{\mathrm{K}^+} = -\ 16{,}000 \pm 4000 \text{ cals.}, \\
W_{\mathrm{K}^+} - W_{\mathrm{Rb}^+} = -\ \ \ 6000 \pm 4000 \text{ cals.}
\end{array}
$$

These values agree fairly well with those calculated from the lattice energy data.

The values for the heat of hydration of individual gas ions can be calculated from a knowledge of absolute electrode potentials. Born[2] has compiled a table for heats of hydration of individual gas ions.

TABLE XXXVIII

Heats of Hydration of Gas Ions

Ion	ΔH	Ion	ΔH
H^+..........	− 262,000 cals.	Cs^+.........	− 74,000 cals.
Li^+.........	− 110,000	Cl^-.........	− 77,000
Na^+.........	− 103,000	Br^-.........	− 68,000
K^+..........	− 82,000	I^-...... .	− 57,000
Rb^+.........	− 73,000		

---

[1] *Ber. deut. physik. Ges.*, **20**, 712 (1918).

[2] *Ber. deut. physik. Ges.*, **21**, 679 (1919).

These values are, however, still tentative and much work remains to be done in this field before completely satisfactory values are obtained.

HEAT OF EVAPORATION OF ELECTRONS

An isolated hot solid in equilibrium with its electron atmosphere is the system to be considered. There are n electrons per unit volume in this atmosphere, exerting a definite pressure p. The relation between this pressure p and the temperature T can be calculated from the second law of Thermodynamics,

$$dS = \frac{1}{T}(dU + dW).$$

The change in internal energy of the electron atmosphere is $nv\phi$, where ϕ is the change in internal energy of the system accompanying the transfer of an electron from the hot solid to the enclosure and v is the volume of the enclosure. Hence,

$$\begin{aligned} dS &= \frac{1}{T}\left[d(nv\phi) + pdv\right] \\ &= \frac{1}{T}\left[v\frac{\partial(n\phi)}{\partial v}dv + n\phi dv + v\frac{\partial(n\phi)}{\partial T}dT + pdv\right]. \end{aligned}$$

Hence,

$$\frac{\partial S}{\partial v} = \frac{1}{T}\left[v\frac{\partial(n\phi)}{\partial v} + n\phi + p\right]$$

and

$$\frac{\partial S}{\partial T} = \frac{v}{T}\frac{\partial(n\phi)}{\partial T}.$$

Since the entropy of the system is a complete differential,

$$\frac{\partial^2 S}{\partial T\partial v} = \frac{\partial^2 S}{\partial v dT},$$

$$\frac{\partial^2 S}{\partial v\partial T} = -\frac{1}{T^2}\left[v\frac{\partial(n\phi)}{\partial v} + n\phi + p\right] + \frac{1}{T}\left[v\frac{\partial^2(n\phi)}{\partial v\partial T} + \frac{\partial(n\phi)}{\partial T} + \frac{\partial p}{\partial T}\right],$$

and

$$\frac{\partial^2 S}{\partial T\partial v} = \frac{1}{T}\left[\frac{\partial(n\phi)}{\partial T}\right] + \frac{v}{T}\left[\frac{\partial^2(n\phi)}{\partial T\partial v}\right],$$

whence

$$-\frac{1}{T^2}\left[v\frac{\partial(n\phi)}{\partial v} + n\phi + p\right] + \frac{1}{T}\frac{\partial p}{\partial T} = 0.$$

Since the electron atmosphere is treated as a perfect gas

$$\frac{\partial(n\phi)}{\partial v} = 0,$$

then

$$T\frac{\partial p}{\partial T} = n\phi + p;$$

now

$$p = nkT,$$

where k is the Boltzmann gas constant and hence

$$\frac{\partial p}{\partial T} = nk + kT\frac{\partial n}{\partial T}.$$

By substituting this value in the previous equation and integrating

$$n = Ae^{\int^T \frac{\phi}{kT^2}dT}.$$

From kinetic theory considerations the number of electrons condensing on a unit surface in unit time is given by

$$N = n\sqrt{\frac{kT}{2\pi m}},$$

where m is the mass of an electron and hence

$$N = A\sqrt{\frac{kT}{2\pi m}}e^{\int^T \frac{\phi}{kT^2}dT},$$

and the saturation photoelectric current per unit area corresponding to any given temperature of the hot body is given by

$$i = A\epsilon\sqrt{\frac{kT}{2\pi m}}e^{\int^T \frac{\phi}{kT^2}dT}$$

or, if ϕ is assumed to be independent of temperature,

$$i = A\epsilon\sqrt{\frac{kT}{2\pi m}}e^{-\phi/kT},$$

where ϵ is the elementary charge of electricity.

Richardson and Cook[1] have developed a method for measuring directly the quantity ϕ which is the heat of evaporation per electron. The experimental arrangement, as given by them, consists of a Wheatstone bridge one arm of which contains the filament under consideration. A number of special precautions have to be taken to avoid troublesome disturbances such as the action of the thermionic current in upsetting the balance of the bridge. For full details the reader is referred to the original paper.

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[1] *Phil. Mag.*, **25**, 624 (1913).

In the experiments, the temperature of the filament was controlled by the current in the Wheatstone bridge. The electrons emitted from the filament flow to the cylinder; by reversing the potential between the filament and the cylinder, the thermionic current could be suppressed. If T and T_0 are the temperatures of the filament and leads respectively, then the total loss of heat from the filament due to the thermionic current is

$$n[\phi + \tfrac{3}{2}k(T - T_0)],$$

where $\frac{3}{2}nkT$ is the kinetic energy of the electrons after leaving the filament and $\frac{3}{2}nkT_0$ is that of the electrons flowing in from the leads.

In carrying out the experiments the current was first measured which was required to keep the filament at a definite temperature with no electron emission and then the current determined to keep the filament temperature constant with the thermionic current flowing.

Let R = resistance of the filament.
i = current flowing through the filament with no electron emission.
$i + di$ = current flowing with electron emission.

Then,

$$R(i + di)^2 - Ri^2 = 2Ri\,di$$

is the additional heat required to compensate for the heat lost by emission. Equating these two quantities

$$2Ri\,di = n[\phi + \tfrac{3}{2}k(T - T_0)],$$

in which all the terms are known except ϕ.

Table XXXIX gives a series of values obtained where ϕ is expressed in equivalent volts.

TABLE XXXIX

Substance	ϕ
Tungsten	4.45
Tantalum	4.17
Osmium	4.3
Molybdenum	4.51
Carbon	4.51

The same authors have also developed a method for measuring the heat of condensation of electrons[1] which can be used for metals of low melting point, but the probable errors are much larger and the results not so satisfactory as in the above.

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[1] *Phil. Mag.*, **20**, 173 (1910).

CHAPTER VII

THE LAWS OF DILUTE SOLUTIONS

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The present chapter is devoted to a consideration of those generalizations which have been found to exist between the magnitude of certain (colligative) properties common to all solutions and the effect on these properties of changing composition of the solution. While the relations that exist among these properties for a given solution are such that, knowing the magnitude of one, under fixed temperature and pressure conditions, the others may be calculated by the use of the principles of thermodynamics, the effect of changing composition is much more complicated, and while the general effect of changing composition is qualitatively the same in all cases, this effect is by no means capable of the same exact mathematical treatment as are the mutual relations existing among the other properties of solutions alluded to above. It will, therefore, be necessary to realize that the application of thermodynamics to the colligative properties of solutions is capable of concise statement only in such cases where the effect of changing composition on these properties is capable of quantitative expression, i e., in the case of the so-called "perfect" or "ideal" solutions.

A perfect solution is one in which the volume change accompanying a small dilution is additive, and no effect is noted other than the alteration of the volume of the solution, similar, in a way, to the change of volume of a perfect gas when it expands into a vacuum. The absence of any heat effect on dilution is a good criterion that a solution is ideal. The deviation of a solution from ideality depends on the nature of the constituents of the solution, the solute and solvent, and on the concentration of the solution. Increased dilution, in general, causes all solutions to approach the ideal condition, the nature of the components determining to what extent dilution must be increased before ideal conditions are realized. This range of concentration over which the relations derived for ideal solutions may be expected to hold will, therefore, vary with the nature of the individual substances concerned. In many cases, it will be found that perfect solutions are not realized at greater concentration than 0.01 M (in some cases at much smaller concentrations), while for some, practically perfect solutions may be formed at much greater concentrations. In order to treat the subject in a general way, it will be necessary to limit consideration to perfect solutions, so that the present chapter is limited to a discussion of *dilute* solutions formed when only two substances are present in the solution. In order to simplify the conditions as much as possible, it is further assumed that only one of these constituents is volatile and the vapor phase is composed of molecules of this constituent only.

Definition: A solution is a one-phase system consisting of two or more molecular species not transformable one into the other. It is, therefore, a homogeneous physical mixture of the various molecular species in question. Not every pair of substances will form a solution to a noticeable extent when they are brought in contact, and the extent to which they will mix to form such a solution will vary greatly with the nature of the substances concerned. Further, as we shall see, the extent to which solution takes place is so varied that substances ordinarily considered insoluble will show, on close inspection, some evidence of solubility. Our ideas of soluble and insoluble substances are therefore relative. For example, water and mercury, when shaken together, will soon separate as a two-phase system and the mixture is not a solution. Water and alcohol, on the other hand, will form a single-phase system when they are mixed in any proportions whatever. These two pairs of liquids represent qualitatively the extremes as regards solubility. Others, such as water and benzene, occupy an intermediate position as regards solubility, and will usually give rise to a two-phase system. Each phase will be found homogeneous and will contain a measurable amount of each constituent. One phase will contain a small amount of water dissolved in a large amount of benzene; the other will contain a small amount of benzene dissolved in a large amount of water. Each phase is, therefore, a solution according to the above definition. In most cases, especially solid-liquid mixtures, solution occurs only to a limited extent, as in the case of sugar and water, and the solution is said to be saturated (when this limit is reached).

From the recent work of Baker[1] it is not unreasonable to expect that solution actually may take place to a limited extent in many cases where the substances are usually regarded as insoluble, but the amount required to produce saturation is so small that it is measurable only indirectly by the change produced in certain properties of the pure solvent. For instance, water is not regarded as soluble in mercury, but by taking extreme care to remove all traces of water from mercury, Baker has found the boiling point of the mercury may be raised considerably above its ordinary boiling point. We should therefore realize that solubility is a universal property of all substances varying in extent from an immeasurably small, though effective, amount to an infinitely great amount. In general, the more closely the constituents are related chemically, the greater will be their mutual solubility. However, this has no bearing on the definition of a solution as given above. Mercury may not be capable of dissolving water to a measurable extent but the small amount taken up would be a solution of water in mercury. In the same way water and benzene mutually dissolve to only a limited extent, giving a two-phase system, each phase being a solution.

If this two-phase system water-benzene is shaken or stirred vigorously, the phases may be further dispersed, but the result is not a homogeneous phase, nor do the benzene and water remain dispersed after agitation ceases; separation of the two original phases begins and the system soon returns to its original condition with its two phases completely separated. In many cases, when two substances are mechanically dispersed, separation is much slower and may give the impression of permanence; when the dispersion is brought about under the proper conditions and to a sufficient extent, the separation of the constituents of the mixture into two clearly defined phases is so extremely slow that the appearance of permanence is very deceptive. Nevertheless, with sufficient time and care in the examination of such cases, it can usually be shown that separation is actually in progress and the dispersion is not permanent. Such solutions are known sometimes as pseudo-solutions or more generally as "Colloidal Solutions." Such cases do not come within the definition of solutions given above. They are neither molecularly dispersed systems nor *permanent*, and, hence, may not be treated in the same comprehensive way as true solutions. In addition to the condition that a solution contains its constituents molecularly dispersed as a homogeneous phase, the system once produced is permanent. It will therefore form spontaneously when the constituents are brought into material contact. This is a fundamental distinction, since, like all processes which occur spontaneously without the application of outside influences, it may be made, by use of a suitable mechanism, to yield a certain amount of useful work, or, conversely, such a solution having once been produced, a definite amount of work must be expended to separate its constituents. The calculation of the maximum work so obtainable makes possible the application of thermodynamics to the study of solutions. This clearly differentiates solutions from such colloidal solutions where the natural change is in the reverse direction. For example, a colloidal solution may be formed, but careful observation (color change, change of viscosity, etc.) shows that the system is undergoing change and, finally, the change progresses to such a degree that close inspection reveals a lack of homogeneity. Colloidal solutions contain constituents highly dispersed in one another; they are not molecularly dispersed, however,[1] and are intermediate between true solutions and coarse suspensions that are evidently heterogeneous.

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[1] *J. Chem. Soc.*, **121**, 568 (1922).

Reference has been made above to the constituents of a solution. By this term is meant any one of the pure chemical substances whose molecular dispersion results in the formation of a solution. With the exceptions noted below, each chemical substance furnishes but one kind of molecule and the constituents of a solution indicate the different molecular species which occur in a solution. Associated substances, such as water, and many other oxygen compounds such as the alcohols, are recognized as pure substances since, while they furnish more than one molecular species (water, for example, being an equilibrium of the molecular species H_2O, $(H_2O)_2$, $(H_2O)_3$ and perhaps others), this equilibrium is established so rapidly that there is no experimental evidence of water having variable properties under the same conditions. Such substances are treated as pure substances having the molecular composition of the vapor phase; in the case of water, as being composed of H_2O molecules, since this is the molecular composition of the vapor phase.[1]

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[1] Zsigmondy's colloidal gold has been shown by Scherrer (*Kolloidchemie*, Zsigmondy, p. 405, Fourth Edition, Leipzig, 1922) to consist of particles containing 380 atoms. Such particles are small, viewed from the standpoint of colloid chemistry; they are evidently far from being molecularly dispersed.

Classification: The three physical states of matter, solid, liquid and gaseous, which we have in the case of pure substances, extend also to solutions so that this subdivision of solutions is both natural and convenient.

Gaseous Solutions: In the case of gaseous solutions the molecules are so far apart that, in the absence of chemical action, they are in most cases practically without influence on each other, as shown by the absence of heat effects on mixing and the relatively small effect when they are allowed to expand into a vacuum. Under such circumstances the physical properties are related to those of the constituents in the simplest way. In the first place, owing to the small mutual attraction of molecules in the gaseous condition, gases mix in all proportions to form true solutions. It is not surprising to find that in gaseous solutions each constituent retains its physical properties unchanged and most of the physical properties of such solutions are therefore additive and may be expressed simply as the sum of the magnitudes of each constituent with respect to the property in question.

Thus, if we consider the magnitude P of any such property of a gaseous solution, it may be simply expressed as follows:

$$P = P_{0A}N_A + P_{0B}N_B + \cdots,$$

where P_{0A}, P_{0B}, $\cdots$ are the magnitudes per mole of the gases A, B, $\cdots$ and N_A, N_B, $\cdots$ are the moles of the individual molecular species A, B, $\cdots$ present in the solution. Dalton's law of partial pressures is an illustration of the application of this relation. Other physical properties may be similarly expressed. The properties of gaseous solutions may be treated satisfactorily by the application of the gas laws and the above relationship.

Solid Solutions: In certain cases two solids may form physical mixtures that are homogeneous and therefore must be classed as solutions. As examples of this type of solution there are certain mixed crystals and certain alloys.[2] Equilibrium in such systems is reached with great slowness and, consequently, measurements are made very uncertain on account of the uncertainty as to what represents the true state of equilibrium. The laws of solutions may be applied here only as an approximation. The same is true to a large extent in certain cases of liquid solutions with high viscosity.

Liquid Solutions: Liquid solutions are by far the most important as most chemical reactions are brought about in liquid solutions both in the laboratory and in nature. An enormous amount of work has been done in order to gain a knowledge of the physical behavior of the constituents of liquid solutions as this must form the basis for the interpretation of the conduct of these constituents under all circumstances. Practically all that follows is therefore written from the standpoint of such solutions.

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[1] Kendall, *J. Am. Chem. Soc.*, **42**, 2477 (1920). Menzies, *ibid.*, **43**, 851 (1921).

[2] van't Hoff, *Z. physik. Chem.*, **5**, 322 (1890).

Composition of Solutions: Mention has already been made of the constituents of a solution, meaning thereby the chemical substances the intermingling of whose molecules forms the solution. Thus, sugar, when brought in contact with water, dissolves and continues to exist as sugar in the solution, from which the sugar may be recovered unchanged. Sugar and water are here the constituents of the solution and the molecules of sugar and the molecules of water are the molecular components of the solution. An arbitrary distinction is nearly always made between the constituents, chiefly on account of the fact that in most cases the solubility is limited. Thus, in the case of sugar and water, solution will take place only to a limited extent and the solution is then said to be saturated. When this occurs, there will be an excess of water in the solution but little if any of the water will dissolve in the excess sugar. Water is said to have a solvent action on sugar and water is referred to as the solvent and sugar as the dissolved substance or solute. These terms are used in this way generally for solutions formed from liquids and either gases or solids, the liquid constituent being termed the solvent and the other constituent the solute. In many cases, especially when dealing with two liquids, the distinction is quite arbitrary. For example, water and alcohol mix in all proportions and the distinction between solute and solvent might be reversed or lose its significance. Again, two liquids, such as benzene and water, form two layers in which the relative quantities of the two constituents are reversed. In such cases the solvent is usually the constituent present in larger quantity. This distinction of solvent and solute is largely for convenience as there is no theoretical distinction, except that, in dilute solutions, the solvent is practically a continuous phase in which the solute is molecularly dispersed. We could therefore distinguish the two constituents of a solution on this basis as the continuous and dispersed constituents.

Method of Expressing Composition of Solutions: The early method of expressing composition in terms of the percentages by weight of the various constituents of a solution, though convenient for analytical purposes, is nevertheless unsuited for theoretical considerations. As we shall see later, the properties of solutions which we shall consider are determined, not by the relative weights of the substances present, but rather by the relative number of molecules of the constituents present in the solution. Such properties of solutions have been designated by Ostwald as colligative properties. It is therefore evident that the logical and convenient method of expressing the composition of a solution is in terms of gram molecular weights or moles. This method of expressing composition shows its value, as we have seen, in expressing the physical properties of gaseous solutions. The mol-fraction method of expressing the composition of solutions is explainable as follows: if a solution is composed of N_A gram moles of constituent A and N_B gram moles of constituent

B, the mol-fraction for the constituent A would be $\frac{N_A}{N_A + N_B}$ and for the constituent B, $\frac{N_B}{N_A + N_B}$. The expressions $\frac{N_A}{N_A + N_B}$ and $\frac{N_B}{N_A + N_B}$ are usually written X_A and X_B respectively. X_A and X_B are then the mol-fractions of the respective constituents, or the amount per unit of solution. The amount of a substance may be expressed in moles, equivalents or formula weights per liter of solution. Another system expresses these same quantities in terms of 1000 grams of solvent instead of 1000 cc. of solution. Concentrations expressed in terms of 1000 cc. of solution and using the above methods of expressing the amounts of substances are known as molal, formal or normal concentrations. When 1000 grams of solvent is made the basis of calculating concentration, we have the composition expressed as weight-molal, weight-formal or weight-normal concentration.

The method of expressing the composition of solutions in terms of molal concentrations would be preferable provided we had a satisfactory kinetic expression for the colligative properties of solutions; while there undoubtedly is a kinetic basis for these phenomena, it has not yet been possible, owing to the complexity and changing nature of solutions with changing conditions, to obtain a general kinetic expression for the behavior of solutions. The effect of composition of solution on the colligative properties can be best expressed as a function of the mol-fraction composition, and, for this reason, this method of expressing the composition of solutions is used in the following discussion.

Colligative Properties

Let us now consider the interrelationships existing between the various colligative properties of solutions—vapor pressure, boiling points freezing points and osmotic pressure. The quantitative relationship existing among these properties is, as stated at the beginning of this chapter, such that, starting with an expression for any one of them, we are able to derive expressions for the others. These expressions, including the effect of composition, cannot all be derived on a purely thermodynamic basis. We must start with some empirical fact (the experimental basis of which, however, leaves us no concern as regards its validity), on the basis of which we derive an expression for the property in question and from which, in turn, we are able by purely thermodynamic reasoning to develop the expressions for the other properties. The development of a theory of solutions begins with the work of van't Hoff[1] who indicated the analogy existing between the laws of solutions and those of gases. The existence of this analogy has led to the conception of a kinetic basis for the treatment of the subject which we shall first consider. Though van't Hoff merely indicated the kinetic origin of osmotic pressure in a qualitative way, a complete kinetic theory of dilute solutions has been developed by other investigators.[1]

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[1] *Z. physik. Chem.*, 1, 181 (1887); Ostwald's Klassiker, No. 110; J. H. van't Hoff, Sein Leben und Werken, by E. Cohen, Leipzig, 1912; *Ber.*, 27, 1 (1894).

In the following section we shall discuss the elementary considerations of the laws of dilute solutions.

Vapor Pressure Lowering: If we consider a liquid and its vapor above it, there must exist a definite relationship between the distribution of any definite molecular species between the two phases, liquid and vapor. Since the pressure of a gas is proportional to the number of particles present per unit volume, the vapor pressure of a liquid due to any molecular species present will be proportional to the number of particles of this molecular species present in the liquid. Expressed mathematically,

$$p = kx_0,$$

i e., the vapor pressure of a liquid, p, is proportional to x_0, the mol-fraction of the liquid existing in the form of the molecular species which gives rise to the vapor pressure, p. If we consider a pure liquid in which the same molecular species exists in both the liquid and vapor phase,[2] this fraction x_0 becomes equal to unity, and k, the proportionality factor, equals the vapor pressure of the pure liquid which we may express by p_0. Our equation then becomes

$$p = p_0x_0,$$

which is the simplest expression of Raoult's law [3] for vapor pressure lowering and states that the vapor pressure of a solution is proportional to the mol-fraction of the solvent present in the solution. As is evident from the above considerations, p is the vapor pressure due to a definite molecular species present to the extent of the fraction x_0 in the solution and does not indicate, for example, the vapor pressure that would result if the molecules of the solvent in the vapor phase were dissociated. Subtracting both sides of the above equation from p_0 and dividing by this term, we obtain the expression

$$\frac{p_0 - p}{p_0} = x = \frac{N}{N_0 + N},$$

where x will be the mol-fraction of the solute present in the solution. The term, N, refers to the moles of solute present, having the molecular weight of the solute in the solution, while N_0 is the number of moles of solvent present having the molecular weight of the solvent in the vapor state.

Henry's Law: Raoult's equation developed above deals with the vapor pressure of the solvent only. We have, by a more general application of the principle underlying Raoult's law, an expression for the vapor pressure of a volatile solute (gas) in a solution, which expression is known as Henry's law. This law states that the vapor pressure of any chemical substance present in a solution is proportional to its mol-fraction or

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[1] L. Boltzmann, *Z. physik. Chem*. 6, 474 (1890), 7, 88 (1891), E. Riecke, *ibid.*, 6, 564 (1890), H A. Lorentz, *ibid*., 7, 36 (1891), L. Natanson, *ibid*., 30, 681 (1899), M. Reinganum, *Boltzmannfestschrift*, Leipzig. 1904, G Jaeger, *Wien. Ber.*, (IIa) 22, 979 (1913); P. Langevin, *J. Chim. Phys.*, 10, 524 (1912).

[2] In the case of a solvent like water, where we have an equilibrium in the liquid phase between the molecular species as represented by the relation $(H_2O)_3 \rightleftharpoons (H_2O)_2 \rightleftharpoons (H_2O)$, it can be shown, from the mass action law, that the same relationship is true.

[3] Raoult, *Compt. rend.*, 104, 1430 (1887); *Z physik. Chem*, 2, 353 (1888).

$$p = kx,$$

where k is a proportionality constant Since the vapor pressure of a substance is merely a measure of its concentration in the vapor state, we can express Henry's law for dilute solutions of gases in liquids in the form

$$c/p = k,$$

which states that the distribution of a gaseous substance between the liquid and gaseous phases is a constant. In this equation, c represents the concentration of the dissolved substance $\left(\text{since } \frac{N}{N_0 + N} \text{ for very dilute solutions is substantially equal to } \frac{N}{N_0} \text{ or the concentration } c\right)$, and p the vapor pressure corresponding to this concentration.

Henry's law has been rigidly investigated over a wide pressure range to determine the extent of its applicability.[1] Sackur and Stern have shown that in the case of carbon dioxide in various organic liquids the behavior of the dissolved carbon dioxide is more nearly in accord with the ideal laws than that remaining in the gaseous condition. In expressing Henry's law, it has also been found that a greater constancy of the coefficient, k, is obtained if we use Ostwald's coefficient for expressing solubility. In this system, we express k as the ratio of the concentration in the solution and in the gas phase, employing data for the density of the solution.

Distribution Law: An expression for the distribution of a substance between two non-miscible solvents can be derived from Henry's law. If a substance whose concentration is C_A in the liquid A has a vapor pressure p, then according to Henry's law

$$\frac{C_A}{p} = k_1.$$

Similarly, if its concentration in the liquid B is C_B, since the partial pressure p must be the same over both phases,

$$\frac{C_B}{p} = k_2$$

and

$$\frac{C_A}{C_B} = \frac{k_1}{k_2} = k,$$

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[1] Sander, *Z. physik. Chem.*, **78**, 513 (1912). Sackur and Stern, *Z. Elektrochem.*, **18**, 641 (1912).

which states that the distribution of a substance between two non-miscible solvents is constant, at any definite temperature, regardless of the initial concentrations employed.

This same relationship also follows from the perpetual motion principle which may be applied by a consideration of the conditions shown in the accompanying diagram (Fig. 1). If we have two immiscible liquids, A and B, in which a volatile substance is dissolved at some definite temperature, the partial vapor pressure of this substance must, at equilibrium, be the same over A and B, for, otherwise, perpetual motion would result by the movement of the vapor from the region of higher to lower vapor pressure where, due to the disturbance of the existing equilibrium, it would dissolve, pass into the second liquid and so maintain a difference in vapor pressures. Perpetual motion being assumed, as a result of experience, to be impossible, the vapor pressure of the dissolved substance must, therefore, be the same over both liquids.

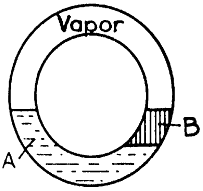

Fig. 1

This method of proof, due to Ostwald, can be similarly applied to a great number of other cases. In general, it can be applied to show that if any two phases are both in equilibrium with a third phase, they are in equilibrium with each other.

By a similar consideration, Ostwald has shown that osmotic pressure must be independent of the type of membrane used, regardless of the mechanism of the process of osmosis.

As is evident from its method of derivation, the relationship, $\frac{C_A}{C_B} = k$, for the distribution of a substance between two phases, A and B, is only valid if the substance has the same molecular structure in both phases. If, however, it exists as the simple molecule, M, for example, in the phase A, and as an associated molecule $(M)_n$ in the phase B, a corresponding relation can be derived.

If we represent the process of association by the equation

$$nM = (M)_n,$$

it follows, from the mass action law, that

$$\frac{(M)_n}{(M)^n} = K \qquad \text{and} \qquad (M) = \sqrt[n]{\frac{(M)_n}{K}}.$$

If we then express the concentration of the substance (M) in terms of its associated form $(M)_n$, we obtain

$$\frac{C_A}{\sqrt[n]{\frac{(C_B)}{K}}} = k,$$

where C_A will be the concentration of the non-associated form in the phase A, and C_B the concentration of the substance in the phase B, where it is associated and has a molecular weight n times that in A. Combining the two constants, we obtain

$$\frac{C_A}{\sqrt[n]{C_B}} = K',$$

which is our desired relationship.

Raising of the Boiling Point: The boiling point of a liquid being defined as the temperature at which its vapor pressure equals the opposing pressure of the atmosphere, it follows that the boiling point of a pure liquid must be raised by the addition of a non-volatile solute, since this brings about a lowering of its vapor pressure. We can derive the relation between this increase in boiling point with decreasing vapor pressure by considering the effect of temperature on the vapor pressures of solvent and solution as in the accompanying diagram in which the curves AC and DG (congruent for dilute solutions) represent the change of vapor pressure, with temperature, of solvent and solution respectively. The abscissæ of the points B and E will be their respective boiling points, under a pressure, P_0, equal to 760 mm. of mercury, which we shall denote by the symbols T_0 and T. Considering the geometrical relationships of the figure over an infinitesimal range, in which case the curves may be treated as straight lines, we have

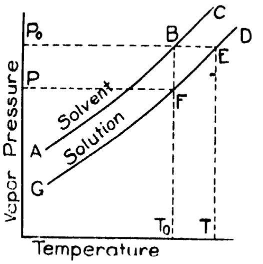

Fig. 2

$$\frac{BF}{BE} = \frac{p_0 - p}{T - T_0} = \tan \angle BEF = \text{slope of curve } DG.$$

Since the curves may be considered as parallel over a small range, the fraction $\frac{p_0 - p}{T - T_0}$ is also the slope of the curve AC. Expressed in terms of differentials, this gives

$$\frac{dp_0}{dT_0} = \frac{p_0 - p}{T - T_0},$$

and, substituting for $p_0 - p$ its value p_0x in Raoult's equation so as to introduce the effect of concentration, we obtain

$$T - T_0 = \frac{p_0}{\frac{dp_0}{dT_0}} x,$$

or

$$\Delta T = B_0 x = B_0 \frac{N}{N_0 + N},$$

which, for dilute solutions, becomes

$$\Delta T = B_0 \frac{N}{N_0}.$$

This equation states that the rise in boiling point of a solution is proportional to the mol-fraction of solute present. The constant B_0, known as the boiling-point constant, represents the relation between the vapor pressure of the solvent and the change in vapor pressure of the solvent with temperature and may be calculated from these, or from its equivalent in the approximate Clapeyron-Clausius' equation

$$\frac{dT_0}{\frac{dp_0}{p_0}} = \frac{RT_0^2}{\Delta H},$$

in which ΔH denotes the molal heat of vaporization of the solvent at its boiling point, T_0. B_0 also denotes the boiling-point rise per mole of solute in one mole of solvent and may thus be directly determined. Instead of this constant, the molal boiling-point constant which refers to the rise in boiling point produced by 1 mole in 1000 grams of solvent is usually recorded and used in the literature.

The Lowering of the Freezing Point: The fact that solutions (sea water for example) freeze at a lower temperature than the pure liquids has long been observed. Blagden[1] first showed that the lowering of the freezing point was proportional to the concentration and this relationship is therefore referred to as Blagden's law. Just as in the case of the boiling point, we can arrive at a relation between the vapor pressures and freezing points of solvents and solutions, and, by applying the Raoult relation between vapor pressure lowering and concentration, express the lowering of the freezing point in terms of the concentration of the dissolved substance.

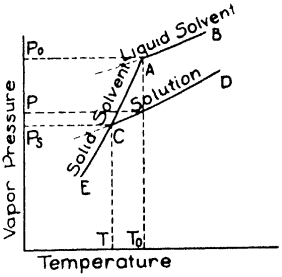

Fig. 3

The freezing point of a solution is defined as that temperature at which the solid solvent can exist in equilibrium with the solution. If we represent the change of the vapor pressure of a pure liquid solvent, solid solvent, and its solution as in the accompanying diagram (Fig. 3), we can derive a relationship by geometrical considerations as was done above in the case of the boiling point. AB represents the vapor pressure of pure solvent, CD that of the solution in *which the mole-fraction of solute is x and AE that of the solid solvent. The intersection points, A and C, of the last curve with the others are the freezing points of solvent and solution respectively.*

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[1] *Phil. Trans.*, **78**, 277 (1788). Ostwald's Klassiker, No. 56 (W. Engelmann, Leipzig, 1894).

It is evident from geometrical considerations of the figure that*

$$\frac{P_0 - P_s}{T_0 - T} \doteq \frac{\partial P_{\text{solid}}}{\partial T}, \tag{1}$$

where $\frac{\partial P_{\text{solid}}}{\partial T}$, the slope of the curve for the solid solvent, gives the change in vapor pressure of the solid solvent with temperature. Also,

$$\frac{P - P_s}{T_0 - T} = \frac{\partial P_{\text{solution}}}{\partial T}, \tag{2}$$

where $\frac{\partial P_{\text{solution}}}{\partial T}$, the slope of the solution curve, gives the change in vapor pressure of the solution with change of temperature. If we assume that the vapor pressure curves for solution and liquid solvent are parallel, i.e.,

$$\frac{\partial P_{\text{solution}}}{\partial T} = \frac{\partial P_{\text{solvent}}}{\partial T},$$

we obtain, by subtracting (2) from (1),

$$\frac{P_0 - P}{T_0 - T} = \frac{\partial P_{\text{solid}}}{\partial T} - \frac{\partial P_{\text{solvent}}}{\partial T}. \tag{3}$$

In order to derive a relation between the freezing-point lowering and mole-fraction analogous to the relation for the rise in boiling point, we must apply the approximate Clapeyron equation, which gives the expressions for the temperature coefficients of the vapor pressures of the solid and liquid solvents:

$$\frac{\partial P_{\text{solid}}}{\partial T} = \frac{\Delta H_s P}{RT^2},$$

where ΔH_s is the molal heat of vaporization of the solid solvent, and

$$\frac{\partial P_{\text{solvent}}}{\partial T} = \frac{\Delta H_l P}{RT^2},$$

where ΔH_l is the molal heat of vaporization of the liquid solvent. Hence,

$$\frac{\partial P_{\text{solid}}}{\partial T} - \frac{\partial P_{\text{solvent}}}{\partial T} = \frac{(\Delta H_s - \Delta H_l)P}{RT^2},$$

where $\Delta H_s - \Delta H_l$ will be the molal heat of fusion, ΔH_0, of the solid solvent. We may therefore write equation (3) as

$$\frac{P_0 - P}{T_0 - T} = \frac{\Delta H_0 P}{RT^2}.$$

Substituting for $\frac{P_0 - P}{P}$ its value in the Raoult equation, we obtain

$$T_0 - T = \frac{RT^2}{\Delta H_0}x \qquad \text{or} \qquad -\Delta T = k_{fp}x,$$

which is our desired relationship.

Osmotic Pressure: The process of osmosis was first observed by Abbé Nollet,[1] who showed that if a solution of sugar be placed in a vessel which is closed below by an animal membrane and dipped in a vessel of water, the latter will diffuse through the membrane and cause the solution to rise in the containing vessel. The phenomenon may be illustrated by the use of the apparatus shown in the accompanying diagram (Fig. 4). A glass vessel A which has a long narrow tube attached to it (a thistle tube serves the purpose) is closed at the bottom by a piece of parchment paper, C, filled with a sugar solution and supported in a vessel of water. The column of liquid in the tube, B, will be seen to rise until the hydrostatic pressure produced just counter-balances the force tending to cause water to enter the vessel. This pressure is known as the osmotic pressure and is caused by the force tending to bring about equilibrium between the pure solvent and solution which in the absence of a membrane results in mixing by diffusion and the production of a homogeneous solution. Osmotic pressure is, then, the excess pressure which must be put on a solution to bring it into equilibrium with the solvent. Between 1826 and 1848 Dutrochet[2] and Vierodt[3] made some quantitative measurements using pigs' bladders as semi-permeable membranes and first recognized the significance of osmotic pressure in physiological processes. Moritz Traube,[4] following the analogy in behavior shown by Graham[5] to exist between animal and colloidal substances, first showed that certain inorganic precipitates of a colloidal nature could act as semi-permeable membranes. Pfeffer[6] first carried out a series of reliable quantitative measurements using porous clay cells in the pores of which was deposited a membrane of $Cu_2Fe(CN)_6$. The modern work of Morse

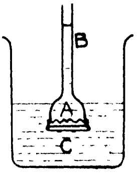

Fig. 4

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[1] Recherches sur les causes de Boullonement des Liquids, Paris, 1748.

[2] *Ann. Chim. Phys.*, [2] **35**, 393 (1827), [2] **37**, 191 (1828); [2] **49**, 411 (1832); [2] **51**, 159 (1832).

[3] *Ann. Phys.*, [2] **73**, 519 (1848).

[4] *Arch. f. Anatomie u. Physiologie*, 1867.

[5] *Phil. Trans.*, **144**, 177 (1854).

[6] *Osmotische Untersuchungen*, Leipzig, 1877.

and Frazer and their students[1] in America, of the Earl of Berkeley and of Hartley[2] in England, and that of other workers[3] have supplied experimental data which have served as a basis for theoretical treatment.

The theoretical treatment of osmotic pressure began with van't Hoff[4] who made use of the experimental data obtained by Pfeffer to confirm his generalizations. Van't Hoff showed that there exists an analogy between the osmotic pressure of a dilute solution and the gaseous pressure that the solute would exert if it existed in the form of a gas in the volume occupied by the solution. As will be seen from the data of Table I obtained by Pfeffer for sugar solutions, osmotic pressure is directly proportional to concentration, a relation corresponding to Boyle's law for gases. Moreover, the change in osmotic pressure with temperature, as van't Hoff showed from Pfeffer's data, is given by the law of Gay-Lussac for gases. van't Hoff showed therefore that the perfect gas equation

TABLE I

THE OSMOTIC PRESSURE OF SUCROSE (PFEFFER)

Concentration in Per Cent	Osmotic Pressure in Atmospheres	Ratio of Osmotic Pressure to Concentration
1	0.686	.68
2	1.34	.67
4	2.75	.68
6	4.04	.67

$$PV = nRT \quad \text{or} \quad P = cRT$$

expressed the relation between osmotic pressure, concentration and temperature. The fact that R has the same numerical value in both equations shows the strict analogy between the two forces. A thermodynamic proof of this relation based on Henry's law will be given later when we discuss the thermodynamic considerations of solutions.

The more accurate measurements of Morse and Frazer, and Berkeley and Hartley showed, however, that these simple relationships may hold reasonably well at high dilution but no longer hold in the case of more concentrated solutions (above 0.2 molar). That this is the case is not at all surprising when we consider that many gases if subjected to pressures equal to the osmotic pressure of dilute solutions would deviate in their behavior from the gas laws on account of mutual attractions between their molecules. Later attempts, therefore, have been made to introduce corrections for these influences in the simple equation given above. A discussion of these theories will be considered in a separate section. An interesting analogy between osmotic and gaseous pressures has been demonstrated by Ramsay,[1] who employed the apparatus shown in the accompanying diagram (Fig. 5). Palladium, at a temperature of 300° C., is permeable to hydrogen but does not allow nitrogen to pass through it and may, hence, be considered as a semi-permeable membrane with respect to a mixture of these gases. A mixture of these gases, rich in nitrogen, is introduced into the palladium bulb *P* which is attached at *J* to the glass tube *M* containing mercury which serves as a manometer to indicate the pressure of the gases in *P*. Let this pressure have an initial value *p*, which is the sum of the partial pressures of the hydrogen, p_{H_2}, and nitrogen, p_{N_2}. If we now enclose the bulb *P* in a gas-tight vessel through which we pass hydrogen under atmospheric pressure, the latter will pass through the palladium until the partial pressure of hydrogen on both sides of the membrane is equal to 1 atmosphere. The total pressure registered on the manometer at equilibrium will therefore be greater than *p*. The excess pressure within the bulb may be considered as the osmotic pressure of the solution of nitrogen in hydrogen when separated from pure hydrogen by a semi-permeable membrane permeable to the latter gas. Whether the osmotic pressure of solutions is similarly brought about by a condition of inequality in pressures due to a difference in concentration of the pure solvent on both sides of the membrane will be discussed more fully when the question of the mechanism of osmosis is considered.

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[1] Pub. No. 198, Carnegie Institution of Washington.

[2] *Phil. Trans.*, **A**, 206, 486 (1906).

[3] Cf. p. 257.

[4] *Z. physik. Chem.*, **1**, 481 (1887).

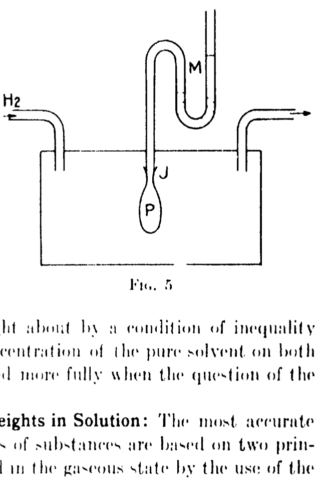

Fig. 5

The Determination of Molecular Weights in Solution: The most accurate determinations of the molecular weights of substances are based on two principles. They may either be determined in the gaseous state by the use of the principle of Avogadro, or in solution by the measurement of any of the colligative properties which we have considered. The experimental details of the latter method will be discussed in the next section and we shall, therefore, limit ourselves here to a consideration of the general applicability of the different methods and their mode of application These relations all express some property of the solution, osmotic pressure, boiling point, etc., as a function of the concentration of the dissolved substance. If we express, then, these concentrations in terms of moles (i e , in terms of the weight of substance dissolved, divided by its molecular weight), we have all the data necessary for computing the molecular weight of the substance in solution. Thus, by expressing the formula for osmotic pressure by the equation

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[1] W. Ramsay, *Phil. Mag.*, [5] 38, 206 (1891). P. Villard, *Compt. rend.*, 126, 1413 (1898). J. Duclaux, *J. Chim. Phys.*, 10, 528 (1912).

$$PV = \frac{m}{M} RT \qquad \text{or} \qquad M = \frac{RTm}{PV},$$

where m is the weight in grams of the substance dissolved in volume V, we can calculate the molecular weight, M, of the substance from the observed osmotic pressure, P. The difficulties involved in the experimental determination of osmotic pressures, however, have prevented its application to the determination of molecular weights except, possibly, in the case of colloids, where the methods of freezing and boiling points are very erroneous.

Molecular Weight Determinations from Vapor Pressure Lowerings: The determination of molecular weights by the lowering of the vapor pressure has been made possible by recent improvements in the mode of measurement of such lowerings. The following results obtained by Menzies[1] illustrate the possible accuracy attainable by such determinations.

TABLE II

VAPOR PRESSURE LOWERINGS OF SOLUTIONS OF NAPHTHALENE IN BENZENE (MENZIES)

Weight of Dissolved Substance in Grams	Volume of Solution in Cc.	Vapor Pressure Lowering	Molecular Weight Obtained
0.3115	48.1	60.1	128.6
0.5118	49.1	105.2	127.5
0.3237	46.1	65.2	128.0
0.5092	46.8	101.6	127.3

The results are seen to agree well with the theoretical value 128.0. The molecular weight is calculated in the above from the formula relating to osmotic and vapor pressures

$$p_0 - p = \frac{P\sigma}{\rho - \sigma},$$

in which p_0 is the vapor pressure of the pure solvent, p of the solution, P the osmotic pressure, ρ the density of the solution and σ the vapor density at pressure p. Assuming the applicability of van't Hoff's law, we can substitute for P its value as derived above and obtain the relation

$$p_0 - p = \frac{mM_0\,760}{M\,1000(\rho - \sigma)},$$

the pressures being expressed in mm. of mercury. In the equation m is the number of grams of solute dissolved in 1 liter of solution, M its unknown molecular weight and M_0 the molecular weight of the solvent in the form of vapor. We thus are able to calculate M by substituting the observed values for the other symbols.

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[1] *Z. physik. Chem.*, **76**, 231 (1911).

The determination of molecular weights from vapor pressure lowerings is especially useful where the freezing-point method is not applicable. Moreover, as it can be applied over a long range of temperature, it can be used to determine the change in molecular weight, as due to association, for example, with temperature.

Molecular Weights from Freezing and Boiling Points: Perhaps the most widely applied method of determining molecular weights in solution has been by means of freezing and boiling points. From the equations for these properties we can determine also the molecular complexity of the substance in solution by seeing what multiple of the commonly accepted molecular weight must be taken to obtain the same value for the constant in these equations as is obtained from the experimental value of the heat of fusion or vaporization. In this way interesting information has been obtained regarding the effect of various solvents on the association of dissolved substances. The solvents of the benzene series, for example, have been found to favor polymerization, whilst the analogues of formic acid tend towards the formation of simple molecules.

Since the present chapter is not intended to consider the case of solutions of electrolytes, mere mention can only be made of the fundamental importance of the study of the colligative properties in connection with the questions of electrolytic dissociation, as, for example, in the modern theories of activity.

Experimental Study of Dilute Solutions

Modern physical chemistry traces its origin from the epoch-making discoveries of van't Hoff, Arrhenius and others in the field of solutions. During the several decades that followed these discoveries the problem of solutions was the chief center of interest, and it is only in the past decade that its numerous offspring—colloidal chemistry, electro-chemistry, etc. have usurped its former prominence. As in other fields, the early experimental studies merely aimed to corroborate and firmly establish the then existing theories and it is only in more recent times that a finesse of technique has been developed which is capable of defining the limits of applicability of the theoretical developments and offering grounds for their alteration and expansion. It is therefore important to have a knowledge of the more reliable experimental methods now available for the investigation of solutions. In the present section a brief description is given of the most refined experimental methods which have been developed for this purpose, together with such other similar measurements as seem of interest, and their applicability to the subject in question will be discussed.

Experimental Determination of Osmotic Pressure. Method of Pfeffer: The first quantitative measurements of osmotic pressure were made by the botanist Pfeffer [1] whose results formed the experimental basis for the theoretical reasoning of van't Hoff.

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[1] Pfeffer, *Osmotische Untersuchungen*, Leipzig, 1877.

The apparatus used by Pfeffer (Fig. 6) consisted of a porous clay cell, *z*, containing the solution to be studied, to which was attached a manometer, *m*, for measuring the pressure developed when the cell was surrounded by pure water. The whole apparatus in position for use is shown in Fig. 7. Pfeffer prepared his cells in the following manner. The clay cell was treated first with a dilute solution of potassium hydroxide and then with a 3 per cent solution of nitric acid, after which it was carefully dried. The wall of the clay cell was then completely filled with water by repeated evacuation under an air pump whilst immersed in water. It was then allowed to stand for some hours in a 3 per cent solution of copper sulphate and filled with the same solution. The interior was then quickly rinsed out several times with distilled water and quickly dried as well as possible by wiping the interior with strips of filter paper. After the cell had stood in the air until the exterior was just moist to the touch, it was filled with a three per cent solution of potassium ferrocyanide and placed again in the copper sulphate solution. After standing thus for one to two days it was closed and allowed to develop what pressure it would by reason of the difference in osmotic pressure between these two solutions. After another interval of from one to two days the cell was opened and filled with a solution containing 1.5 per cent potassium nitrate and 3 per cent copper ferrocyanide Under these conditions a pressure of about three atmospheres is developed. If the cell was to be used for measuring pressures greater than three atmospheres, it was tested under a greater pressure, which is readily done by increasing the concentration of the potassium nitrate in the test solution. It was found desirable to have the initial pressure develop slowly and to allow the cell to be subjected for some time to this low pressure. This slow initial development of pressure seems to have the effect of pressing the membrane material into the cell wall in such a manner that its continuity is not destroyed. If the pressure is allowed to develop rapidly, the manometer shows a rapid initial rise to a maximum, but this pressure soon falls. In such cases, Pfeffer frequently noted that a brown

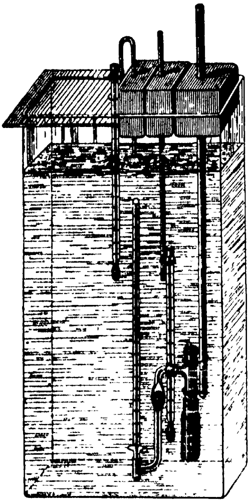


Fig. 6. Pfeffer's Apparatus for Osmotic Pressure Measurement

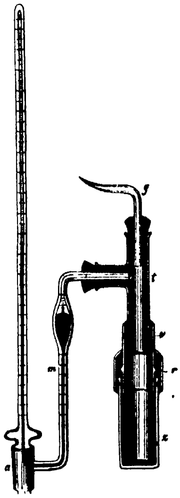


Fig. 7

stain of copper ferrocyanide appeared on the exterior of the cell, showing that the membrane had been ruptured.

Remarkably good success was had by using the above method. Of twenty cells scarcely a failure was recorded, while before resorting to the expedient of partial drying no membrane was successfully deposited on the surface of the cell. For this reason Pfeffer had been compelled in his first investigations to use cells in which the membranes had been deposited at some distance beneath the surface of the cell wall. In order to deposit the membrane in ~~such a position~~, the cell with its wall filled with water was placed in a 3 per cent copper sulphate solution for fifteen to twenty minutes and filled with a solution of potassium ferrocyanide of the same (3 per cent) concentration. When the membrane was formed in this way, by diffusion, it occupied a position near the inner surface of the cell.

Membranes deposited on the surface of a cell, by the method outlined above, not only have the advantage that they are immediately in contact with the solution under investigation, but they are also more easily and successfully formed than when the membrane is formed within the interior of the cell wall. In certain cases membranes could be readily formed on the surface of the cells while successful deposition in the cell wall was either impossible or could be accomplished only with the greatest difficulty, even though the cells in both cases were from the same source. It is interesting to note that Pfeffer found that cells made by only one manufacturer out of the ten whose products were tested gave satisfactory results and that he had at his complete disposal the entire use of a pottery for the solution of his difficulties.

Pfeffer undoubtedly had very reliable cells at his disposal as he found that 15 to 20 per cent solutions of dextrin showed absolutely no leakage of solute after a period of fourteen days, and a 5 per cent solution of sucrose after being kept in the cell twelve days at a temperature of 12°-20° showed no detectable amount of solute in the surrounding solvent. The idea of using $Cu_2Fe(CN)_6$ as a membrane was due to Traube,[1] who had previously shown it to be impermeable to certain dissolved crystalloids while permitting water to pass through it. Pfeffer also used membranes of other materials and carried out measurements with dilute solutions of sugar, dextrose, gum arabic, electrolytes, etc. Lack of accuracy in Pfeffer's results with such solutes as sucrose can hardly be traced to faulty membranes. From his results, he showed that osmotic pressure was proportional to concentration, was much smaller in the case of colloidal substances like gum arabic than with molecularly dispersed systems, and that osmotic pressure increased linearly with temperature.

Method of Morse and Frazer: The two chief problems which confront the investigator who attempts a direct measurement of osmotic pressure are the production of a membrane which is truly semi-permeable and an accurate determination of the pressure produced, with careful control of temperature and accurate analyses of the solutions. If any of these factors is disregarded, it is perfectly evident that no great reliability can be placed on the results. The details of the method of Pfeffer, as is evident from their description, fail in certain respects to provide the necessary refinements and, though the importance of Pfeffer's pioneer work cannot be overestimated, it required the development of innumerable, practically important details to give the method sufficient accuracy over a wide range of concentration to make it applicable to the theoretical problems of dilute solutions.

H. N. Morse, while engaged in the electrolysis of solutions of permanganates with porous diaphragms in order to prepare solutions of pure permanganic acid, noticed, on occasions, the osmotic activity of such cells in whose pores manganese dioxide had separated. This suggested the idea of depositing copper ferrocyanide membranes electrolytically in porous

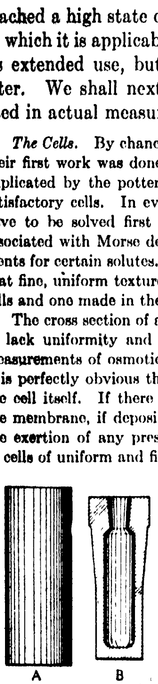
[1] M. Traube, *Zentral. f. mediz. Wiss.*, 1864; *Archiv. Anat. Wiss. Med.*, p. 87 (1867).

clay cells for the purpose of measuring osmotic pressure. The method was described by Morse and Horn[1] in 1901. While the easy formation of an osmotically active membrane by this method was readily obtained, there remained a very great number of experimental details the solution of which was necessary before quantitative measurements could be made. In fact all and more of the difficulties encountered by Pfeffer had to be solved.

Morse and Frazer,[2] therefore, undertook in 1901 an extensive improvement in the mode of measurement of osmotic pressure, utilizing the ~~electrolytic~~ method of Morse and Horn for depositing the membrane. As a result of the improvements in the details of measurement introduced by these investigators in collaboration with their students, the measurement of osmotic pressure has reached a high state of refinement and accuracy in the limited number of cases to which it is applicable. The limit of its applicability, however, has prevented its extended use, but this phase of the problem will be considered in detail later. We shall next describe the various parts of the apparatus which are used in actual measurements.

The Cells. By chance these investigators had at their disposal about 20 cells with which their first work was done. Unfortunately later experience showed these cells could not be duplicated by the potter. Various potteries were called on to assist in the production of satisfactory cells. In every case failure resulted. It was then evident the problem would have to be solved first in the laboratory. After trying various expedients, Frazer while associated with Morse developed a method of fabricating the cell that satisfied the requirements for certain solutes. Microscopic examination of sections of good and bad cells showed that fine, uniform texture was required. Fig. 8 *a* and *b* show sections of one of the potter's cells and one made in the laboratory, respectively.

The cross section of an ordinary porous cell as produced in the industry (Fig. 8 *a*) is seen to lack uniformity and contain numerous air blisters. Since the function of the cell in measurements of osmotic pressure is to secure a support for the semi-permeable membrane, it is perfectly obvious that the fineness of texture of the latter will depend on the pores of the cell itself. If there should happen to be a point where the cell wall is highly porous, the membrane, if deposited at all over this area, must necessarily be held but loosely, and the exertion of any pressure at this point would easily disrupt it. Hence the attainment of cells of uniform and fine texture is necessary.



Cylinder of Pressed Clay Fashioned Cell

FIG. 9

The first step taken was to select two clays of such composition that it would be unnecessary to add any of the ground material used by the potter as a "binder." These were carefully treated to remove coarse particles after which the mixture was molded under pressure into cylindrical form, Fig. 9 *a*, and then the cell was turned on the lathe to the proper size and shape, Fig. 9 *b*, dried, and burned. The upper portion was then glazed to permit attachment of the manometer.

Such cells were entirely satisfactory for measurements with non-electrolytes of high molecular weights. To make them applicable to substances of small molecular weights, the porosity of the cells has recently been further decreased and a more perfect support given

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[1] *Am. Chem. J.*, **26**, 80 (1901).

[2] *Am. Chem. J.*, **28**, 1 (1902); **29**, 173 (1903); **32**, 93 (1904); **34**, 1 (1905); **36**, 1 (1906); **37**, 324, 425, 558 (1907); **38**, 175 (1907); **39**, 667 (1908); **40**, 1, 194, 266, 325 (1908); **41**, 1, 92, 257 (1909); **45**, 91, 237, 383, 517, 554 (1911); **48**, 29 (1912); Publication Carnegie Inst. No. 198.

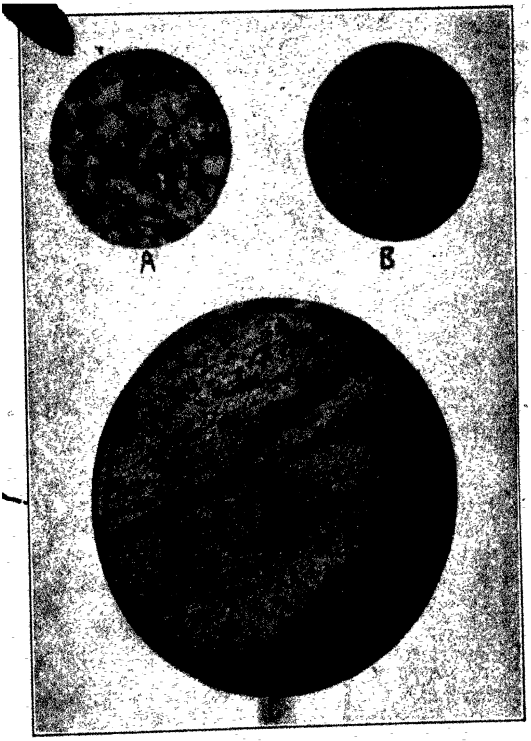

FIG. 8

PHOTO-MICROGRAPHS OF POROUS CELLS

the membrane by the precipitation "in situ" of an inert substance like $MgSiO_3$.[1]

A cross section of such a cell is shown in Fig. 8 c, the dark portion being the precipitated filling. Its opaqueness compared to the rest of the cell shows the fineness of its pores. Such cel[illegible] are efficient supporters of the membrane, allow only a minimal leakage, a rapid [illegible]ent of equilibrium, and require no period of "seasoning." Recent experiments, [illegible] the above-mentioned investigators, however, have shown that the presence of too fine and thi[illegible] a cell may vitiate the results, due possibly to the interference of electrokinetic effects. The presence of a fine capillary system in the cell may bring about a condition of affairs in which the solution proximate to the semi-permeable membrane has a concentration (due to the capillary effect of the cell pores) far different from that of the solution and hence the results obtained, though reproducible and apparently referring to the solution studied, really refer to entirely different conditions.

The desideratum, therefore, is the production of a very fine material on the surface of which the membrane may be deposited and which will present its other surface to the pure solvent, thus obviating any concentration change due to capillary effects.

After its preparation and filling, the cell is boiled in water and all air bubbles removed by continued electrolysis of a 0.05 per cent Li_2SO_4 solution, the water transferred electro-endosmotically serving to remove the last traces of air. The cell, after electrolysis with distilled water to remove the last traces of electrolyte, is ready for the deposition of the semi-permeable membrane.

The Membrane. Despite efforts to find other membranes, the $Cu_2Fe(CN)_6$ first described by Traube has always been most satisfactory for osmotic pressure measurements, and has been exclusively used in these researches. The mode of deposition, however, and the care exercised in its development have been altered.

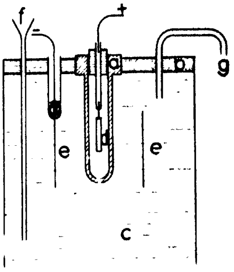

FIG. 10. Apparatus for Membrane Deposition

The mode of deposition of the membrane by the method of Morse and Horn is shown in the accompanying diagram (Fig. 10). The porous cup (*a*) in which the membrane is deposited is held by means of a rubber stopper (*b*) in a glass vessel (*c*) containing a 0.1 per cent solution of $K_4Fe(CN)_6$. The cell is filled with a 0.1 M solution of $CuSO_4$ and a current allowed to pass through the solutions from a copper anode (*d*) held in the porous cup by a rubber stopper. A platinum sheet which surrounds it serves as the cathode (*e*). The funnel (*f*) and exit tube (*g*) serve to renew the $K_4Fe(CN)_6$ solution so as to prevent an accumulation of alkali during the electrolysis.

When the cell is put through the membrane-forming process for the first time, there is a temporary fall of resistance as the cell wall becomes filled with the electrolyte and a rapid rise thereafter as the membrane continues to form. A maximum resistance is soon reached, after which the process should be discontinued and the cell placed in water. After several days, the process is repeated, and, after several repetitions, a good cell will readily develop considerable pressure with a cane sugar solution. It is, however, still imperfect and for complete development may require as much as six months or a year of such treatment. Apparently worthless cells have proved useful with no other treatment than being left in distilled water which is frequently changed.

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[1] Grollman and Fraser, *J. Am. Chem. Soc.*, 45, 1710 (1923).

The Measurement of Pressure. The pressure developed may be determined by reading the volume of a column of nitrogen enclosed in a carefully calibrated manometer, by means of a cathetometer.

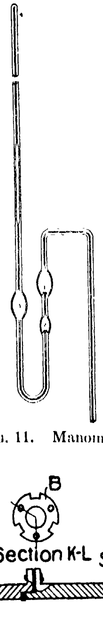

Fig. 11. Manometer

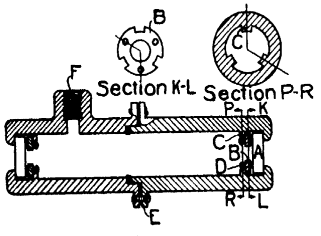

Fig. 12. Cross Section of Interferometer

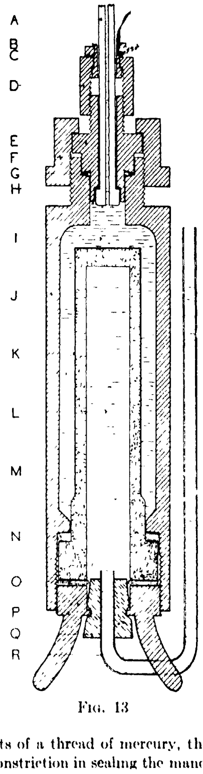

Fig. 13

The upper end of the manometer (4, Fig. 11) consists of a thread of mercury, thus obviating the error of the unknown change in bore due to constriction in sealing the manometer end. The use of glass manometers suffers from the disadvantage that the time for the attainment of equilibrium is long; their accuracy decreases with increased concentration due to deviation of the gas from Boyle's law, occlusion of gas and increased percentage error of readings; and, finally, they are easily broken at high pressures or by temperature changes. Application has, therefore, been made of a resistance pressure gage [1] and of the water interferometer,[2] using the change in the index of refraction due to the pressure exerted in the experiment as a means of measuring this pressure. This apparatus has been further modified [1] to give an increased accuracy and ease of manipulation over the original apparatus. The more recent form is shown in Fig. 12.

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[1] Fraser and Myrick, *J. Am. Chem. Soc.*, **38**, 1907 (1916).

[2] Fraser, Van Doren, Parker and Lotz, *J. Am. Chem. Soc.*, **43**, 2497 (1921).

This instrument has been described by Grollman and Frazer.[2] It has a range of 30 atmospheres. This can be increased by the use of thin glass plates inserted in the path of the beam passing through the non-pressure side.

Since the range of 30 atmospheres corresponds to 3000 divisions on the interferometer and since readings on the latter are capable of duplication within 10 divisions, the pressure readings are accurate to 0.1 of an atmosphere. The accuracy may be increased by the use of a liquid more compressible than water or by the use of a longer pressure chamber and wider windows. The length of the pressure chamber of the instrument used was 80 mm. By arranging the mirrors and prisms of the interferometer so that there is a greater distance between the two beams, larger windows can be used in the pressure gage, which insures more accurate readings.

The older methods of joining the manometer to the cell have been improved by Frazer and Myrick,[3] who devised the apparatus shown in Fig. 13.

"*M* (Fig. 13) is the clay cell with the membrane of copper ferrocyanide *K* deposited on its exterior. This extends only as far as indicated by the heavy line *K*, the neck and shoulder of the cell being glazed to ensure tight joints. *J* is the bronze cylinder into which the cell is fastened by means of the plug *P*. The latter has three legs upon which the apparatus stands and which serve as a means of screwing the plug into the cylinder. *N* is a thick rubber washer and *O* is a piece of commercial 'Rainbow Packing,' about a millimeter and a half thick. This packing gives perfect satisfaction, while the ordinary rubber will not withstand higher pressures. At all other joints *N*, *G*, *H*, the packing is surrounded on all sides so it can not flow, hence in these places the softer rubber washers answer very well. In fact, it is desirable to have *N* and *G* thick (about 4 mm.) and soft so that initial pressure may be secured by their compression

"*R* is a glass U-tube held in the mouth of the cell by means of the rubber stopper *Q*. This is simply to keep the solvent *L* up in the cell and yet leave it open to the atmosphere. *I* is the solution to be measured. *E* is the manometer attachment and is fastened onto the cylinder by means of the nut *F*, *G* being a thick rubber washer described above. *A* is a piece of capillary glass tubing to which the manometer is sealed. The square shoulder at the lower end of *A* is secured by sealing onto a piece of tubing, of the size desired for *A*, another piece, having somewhat larger external dimensions. The joint is kept soft and the glass allowed to flow together until a considerable enlargement is secured, the internal diameter being kept of original size by careful blowing. After cooling, the larger piece of tubing is cut off close to the enlarged joint. *A* is then mounted in the lathe and the enlarged end ground to the desired size and shape. In this manner the lower end of *A* is made to fit accurately into the lower end of *E*, as shown in the diagram To hold *A* in position, *B* is sealed onto *A* by means of sealing wax (Khotinsky) and after putting *D* into position, *C* is screwed onto *B* It will be seen that by turning *D* to the left, *A* is raised and held tightly in position in *E* against the washer *H*. By turning *D* to the right, *A* is lowered and excess solution is allowed to escape This method of joining glass and metal is of general application and has proven most satisfactory. Such a joint will hold tight under any pressure which will not actually break the glass."

In the use of the interferometer cell, a similar attachment is used with the exception that the tube *A* is of brass and the cell contents are separated from the interferometer cell by a mercury trap.

With the above-described apparatus and the great care in the details of carrying out experimental determinations, such as temperature control, analysis, etc., to which reference must be made to the original articles, data have been obtained over a range of temperatures from 0° to 80° and over the complete range of concentrations in the case of sucrose solutions, as well as measurements of mannite, phenol, etc. The results obtained for some of these substances are given in the following tables.

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[1] Grollman and Frazer, *J. Am. Chem. Soc.*, **45**, 1710 (1923).

[2] ***J. Am. Chem. Soc.*, 45, 1714, 1715 (1923).**

[3] ***J. Am. Chem. Soc.*, 38, 1907 (1916).**

TABLE III[1]

OSMOTIC PRESSURES OF SUCROSE SOLUTIONS

Grams Sugar/1000 Cc. of Solution	Grams Sugar/1000 G. of Water	Equilibrium Time, Minutes	Osmotic Pressure, Atmospheres
	30°		
478.3	680	90	57.5
472.0	665	12	56.6
597.0	958	90	87.2
605.4	980	150	90.4
608.5	990	165	92.0
700.2	1260	195	129.5
695.0	1242	225	127.4
781.4	1549	180	169.1
781.4	1549	225	168.6
777.3	1533	90	164.1
831.5	1758	300	(198.2)
826.2	1737	195	200.2
839.8	1796	165	206.1
	55.7°		
477.2	674	22	61.0
481.4	685	20	63.1
610.6	996	35	97.4
612.7	1000	16	98.7
702.3	1270	30	132.4
706.4	1284	55	133.5
782.5	1556	75	170.6
791.9	1590	90	178.7
856.5	1877	120	222.0
842.9	1810	135	213.8
900.2	2112	165	259.3
910.6	2190	135	256.6
No analysis.	. . . .	135	273.0

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[1] Lotz and Frazer, *J. Am. Chem. Soc.*, **43**, 2501 (1921).

OSMOTIC PRESSURE OF SUCROSE SOLUTIONS AT 0°

(Morse, Frazer and Zies)

Concentration (Weight Normal Solutions)	Osmotic Pressure Observed	Ratio of Osmotic to Gas Pressure
.1	2.46	1.11
.2	4.72	1.06
.3	7.09	1.06
.4	9.44	1.06
.5	11.90	1.07
.6	14.38	1.08
.7	16.89	1.08
.8	19.48	1.09
.9	22.19	1.10
1.0	24.83	1.12

TABLE IV[1]

OSMOTIC PRESSURE OF AQUEOUS PHENOL SOLUTIONS AT 30°

O.p. calc. from				O.p. calc. from			
Concn.	Formula $P = \frac{RT}{V_0}\left(x + \frac{x^2}{2} + \frac{x^3}{3} + \cdots\right)$	O.p. obs.	$\frac{\text{Calc. o.p.}}{\text{Obs. o.p.}}$ = degree of assoc.	Concn.	Formula $P = \frac{RT}{V_0}\left(x + \frac{x^2}{2} + \frac{x^3}{3} + \cdots\right)$	O.p. obs.	$\frac{\text{Calc. o.p.}}{\text{Obs. o.p.}}$ = degree of assoc.
0.1	2.46	1.46	1.68	0.6	14.73	7.62	1.93
.2	4.92	2.84	1.73	.7	17.16	8.82	1.95
.3	7.38	3.93	1.88	.8	19.59	10.05	1.95
.4	9.83	5.12	1.92	.9	22.02	11.28	1.95
.5	12.28	6.40	1.92	-	--	-	-

[1] Grollman and Frazer, *J. Am. Chem. Soc.*, **45**, 1707 (1923).

The Method of Berkeley and Hartley:[2] The method of these investigators differs from those hitherto described in that instead of measuring the pressure that is exerted due to diffusion of the solvent into the solution, this diffusion is prevented by the application of a pressure to the solution just sufficient to prevent passage of solvent into the solution.

A cross section of the apparatus is represented in Fig. 14.

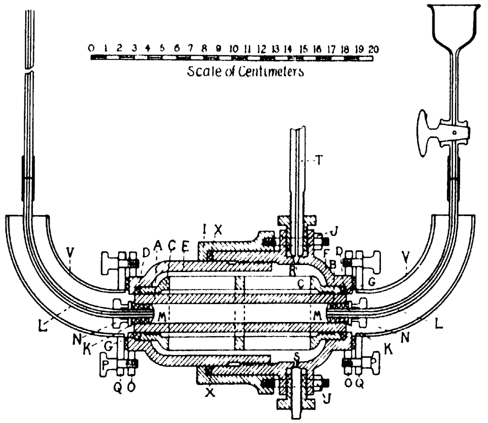

FIG. 14. Apparatus of the Earl of Berkeley and E. G. J. Hartley

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[2] *Phil. Trans.*, **A 206**, 486 (1906).

"*AB* is a porcelain tube 15 cm. long, 2 cm. external and 1.2 cm. internal diameter, the ends of which are glazed. This tube carries the semi-permeable membrane as close to the outer surface as possible. *CC* is a gun-metal cage against the ends of which the dermatine rings *DD* are compressed when the two parts *E* and *F* of the outer gun-metal vessel are screwed together. The ends of this cage have shallow radial grooves cut out of them so as to prevent the dermatine rings from rotating and rubbing the membrane during the operation of screwing *E* and *F* home. The length of the cage is such that, when finally set up, the dermatine rings just overlap the ends of the porcelain tube.

"The outer gun-metal vessel (capacity about 250 cc.) contains the solution which, when a pressure is applied to it, forces the dermatine rings against the bevelled faces *GG*, and thus causes a tight joint to be made with the porcelain tube. The joint between *E* and *F* is made good by another dermatine ring *X*, which is compressed between the metal ring *I* and the nuts *JJ*.

"The ends of *AB* are closed by pieces of thick-walled rubber tubing *KK*, through which the brass tubes *LL* are passed; a water tight joint between *LL* and the inside of the porcelain tube is obtained by compressing the rubber between the metal washers *MM* and the nuts *NN*. The brass tubes are joined by rubber tubing, one to a glass tap and the other to an open glass capillary—the latter, which we shall call the water gauge, was graduated in millimeters and calibrated; one centimeter of the bore contains 0.00312 cc. The outer ends of *E* at *F* have threads cut on them to receive the brass rings *OO*, which in their turn are perforated by screw-holes to receive the thumbscrews *PP*, by means of which, together with a rubber washer, a tight joint is made between the flanges *QQ* of the curved metal tubes *VV* and the ends of *E* and *F*.

"The perforation *R* is for filling the apparatus with solution, and also for connecting to the pressure apparatus, while *S* serves to empty the vessel."

A determination is made by filling the porcelain tube containing the membrane with water, which partially fills the attached capillary tube, surrounding it with the solution to be investigated, and gradually applying a pressure which could be regulated and measured, until there was no flow of water from the interior of the solution. This pressure was determined by observing the rates of movement of the water meniscus in the capillary tubes at pressures near the osmotic pressure. A correction to this reading was applied, due to leakage resulting from imperfect contact between the dermatine rings and the membrane, or from cracks in the glaze. Measurements by the above method are fairly rapid, inasmuch as it is not necessary to wait for equilibrium to set in by a diffusion through the cell, which diffusion is usually slow near the equilibrium pressure.

The same investigators[1] have devised a dynamic method which is based on the measurement of the rate of flow of solvent into the solution which gives results concordant with other methods, if we consider the initial flow only and assume it to be that which would occur if the water were caused to pass through the membrane by the application of a mechanical pressure equal to the osmotic pressure.

Vegard,[2] who has described a simple form of the above apparatus, showed that the rate of flow gradually diminishes and, hence, the initial rate of flow alone gives accurate results. The relation between the velocity of osmotic flow and osmotic pressure has been further investigated by Sebor[3] and Antropoff[4] and is illustrated in the following table (V) by some results from the work of Berkeley and Hartley.[5]

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[1] *Proc. Roy. Soc.*, **A 82**, 271 (1909).

[2] *Phil. Mag.*, [6] **16**, 247, 396 (1908); *Proc. Camb. Phil. Soc.*, **15**, 13 (1909).

[3] *Z. Elektrochem.*, **10**, 347 (1904).

[4] *Z. physik. Chem.*, **76**, 721 (1911).

[5] *Proc. Roy. Soc.*, **A 82**, 273 (1909).

TABLE V

RELATION BETWEEN VELOCITY OF OSMOTIC FLOW AND OSMOTIC PRESSURE

Pressure in Atmospheres	Diffusion Velocity in Mm. of Capillary per Second	Ratio of Diffusion Rates	*Ratio of Pressures*
20.41	0.1075	1	1
40.82	0.2203	2.05	2
61.24	0.3240	3.01	3
81.65	0.4303	4.00	4
102.06	0.5319	4.95	5
122.47	0.6378	5.93	6

Numerous other experimental measurements of osmotic pressure have been made by E. Cohen and J. W. Crommelin,[1] A. Ladenburg,[2] R. H. Adie,[3] G. Tammann,[4] A. Naccari,[5] A. Ponsot,[6] P. S. Barlow,[7] S. Kahlenberg,[8] G. Flusin,[9] W. G. Wilcox,[10] E. Fouard,[11] C. F. Nelson,[12] and A. E. Koenig.[13] Due to the lack of sufficient perfection in the apparatus used by these investigators, however, their results are conflicting and will, therefore, not be further discussed here.

Some of the results of Berkeley and Hartley are given in Table VI which also contains the results obtained by Frazer and Myrick for comparison.

Measurement of Relative Osmotic Pressures: A number of methods have been devised which, though incapable of giving any absolute values, nevertheless furnish us with useful information regarding the relative values of the osmotic pressures of different substances. The cells of plants and animals consist of protoplasm enclosed in walls which, being strong and resistant, maintain their shape and size when immersed in solutions of other substances. These walls are permeable to water and aqueous solutions but are also lined on the inside with a thin membrane which is semi-permeable, allowing only water to pass through it, but no dissolved substances. The Dutch botanist De Vries [14] first applied such cells to the determination of osmotic pressures,

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[1] *Z. physik. Chem.*, **64**, 1 (1908).

[2] *Ber.*, **22**, 1225 (1889).

[3] *J. Chem. Soc.*, **59**, 344 (1891).

[4] *Z. physik. Chem.*, **9**, 97 (1892).

[5] *Atti. accad. Lincei*, **6**, 32 (1897); *Nuovo cim.*, [4] **5**, 141 (1897).

[6] *Compt. rend.*, **125**, 867 (1897); **128**, 1417 (1899).

[7] *Phil. Mag.*, [6] **10**, 1 (1905); [6] **11**, 595 (1906).

[8] *J. Phys. Chem.*, **10**, 141 (1906); **13**, 93 (1909).

[9] *Ann. chim. phys.*, [8] **13**, 480 (1908).

[10] *J. Phys. Chem.*, **14**, 576 (1910).

[11] *Compt. rend.*, **153**, 769 (1911); *J. phys.*, [5] **1**, 627 (1911); **2**, 269 (1912); *Bull. soc. chim.*, [4] **11**, 249 (1912).

[12] *J. Am. Chem. Soc.*, **35**, 658 (1913).

[13] *J. Phys. Chem.*, **22**, 461 (1918).

[14] *Z. physik. Chem.*, **2**, 415 (1888); **3**, 103 (1889).

TABLE VI

OSMOTIC PRESSURE OF SUCROSE SOLUTIONS

Grams of Sucrose in 1000 Cc. of Solution	Grams of Sucrose per 1000 Grams of Water	Osmotic Pressure		
		Berkeley and Hartley		Frazer and Myrick
		P at 0° (Observed)	P at 30° (Calculated)	P at 30° (Observed)
180.1	202	13.95	15.48	15.59
300.2	370	26.77	29.72	29.78
420.3	569	43.97	48.81	47.88
540.4	820	67.51	74.94	73.06
660.5	1133	100.78	111.87	109.10
750.6	1430	133.74	118.46	148.80

using cells from the plants—*Tradescantia discolor*, *Curcuma rubicaulis* and *Begonia manicuta*—which he found most suitable for such work.

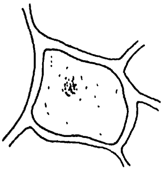

FIG. 15*a*

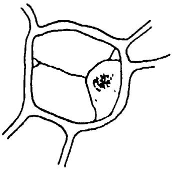

FIG. 15*b*

Fig. 15*a* shows the normal appearance of such cells as seen under the microscope. If now the cell is surrounded by a solution having the same osmotic pressure as the cell contents, it will maintain its normal appearance and the same is true if it is surrounded by a solution of smaller osmotic pressure in which case any distension of the semi-permeable membrane is prevented by the resistant cell wall. If, however, the cell is surrounded by a solution of greater osmotic pressure than its own, water will leave the cell and cause its contents to shrink, giving the appearance of Fig. 15*b*. By determining the lowest concentrations of various substances which are necessary to prevent this contraction of the semi-permeable membrane, we have the relative concentrations necessary to produce the same osmotic pressure. The reciprocals of these isosmotic or isotonic concentrations, when expressed in molar quantities, are known as isotonic coefficients and show the relative osmotic pressures of solutions of equal molecular concentration. Some of De Vries' results are given below (Table VII).

TABLE VII

ISOTONIC COEFFICIENTS OF AQUEOUS SOLUTIONS (DE VRIES)

Substance	Isotonic Coeff.
Glycerol	1.78
Cane Sugar	1.88
KNO_3	3.00
NaCl	3.05
$CaCl_2$	4.33
$MgCl_2$	4.33

These values were of great use in the development of early theories of solution, clearly showing the effect of dissociation of electrolytes on the colligative properties of solutions.

Hamburger[1] has employed red blood corpuscles for the same purpose. The lowest concentrations of various substances necessary to cause the corpuscles of defibrinated deer's blood to settle, leaving a liquid above, have the same osmotic pressure. The results obtained by this method,[2] as well as those obtained in the study of the effect of various substances on the movement of various bacteria,[3] all yield results which agree within the limits of error of the experimental determinations.

The method of Tammann[4] consists in noting the optical results due to diffusion through a semi-permeable membrane of an inorganic material such as $Cu_2Fe(CN)_6$. The slight currents due to diffusion through the membrane are observed by a refractometer and their absence is used to indicate the presence of an isotonic solution.

The Experimental Determination of Vapor Pressure: Of the various experimental studies of the colligative properties, none is more desirable than that of vapor pressure. Of all the colligative properties, vapor pressure and osmotic pressure determinations alone may be made at various temperatures. The fact that, from the values for the former, we may derive the values of the other colligative properties makes this experimental study most desirable. The chief problems are constant temperature regulation, purity of reagents, the removal of all dissolved gases, and a sensitive instrument for pressure mensuration. The experimental methods of measuring vapor pressures are divisible into two types, the static and dynamic. The static method was first applied by von Babo,[5] whose work, together with that of Wüllner,[6] led to the first generalizations on the relation between vapor pressure lowering and concentration. These workers showed that the lowering of the vapor pressure is proportional to the concentration of solute; that, for the same solution, the lowering due to a non-volatile substance is, at all temperatures, the same fraction of the vapor pressure of the pure solvent.

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[1] *Z. physik. Chem.*, **6**, 319 (1890).

[2] W. Löb, *Z. physik. Chem.*, **14**, 424 (1894). H. Koppe, *Z. physik. Chem.*, **16**, 261 (1895). S. G. Hedin, *Z. physik. Chem.*, **21**, 272 (1896).

[3] Wladimiroff, *Z. physik. Chem.*, **7**, 529 (1891).

[4] *Wied. Ann.*, **34**, 299 (1888).

[5] L. v. Babo, Über die Spannkraft des Wasserdampfes in Salzlösungen, Freiburg (1847).

[6] *Ann. Physik*, [2] **103**, 529 (1858); **105**, 85 (1858), **110**, 564 (1860).

The later methods of Tammann[1] and Raoult,[2] though allowing only a limited degree of accuracy, nevertheless led Raoult, as a result of his exhaustive experimental investigations, to the enunciation of his law already discussed. The method of Raoult consisted in introducing a pure liquid into a barometer tube inverted over mercury, a solution with the same liquid as solvent into another similar tube, and then comparing the heights of the mercury column in these tubes with that of a third which was connected to a volume of air of known pressure, all three being connected through a common reservoir to an adjustable mercury container. By use of his simple apparatus Raoult could determine a difference in pressure of 10 mm. of Hg with an accuracy of 2 per cent.

Dieterici[3] first used a differential method for the determination of vapor pressure lowering. This method depending as it does on a direct measurement of the difference in pressures between solvent and solution, instead of absolute measurements of both, is capable of most refined accuracy and all recent methods are based on this principle. Dieterici used the movement of a glass plate (0.08 mm. thick) as measured by its torque effect on a quartz thread which was attached to a mirror as a means of measuring the difference in pressures between solvent and solution. Readings could be made with an accuracy of 0.001 mm. Hg over a range of 0.1 to 0.01 mm. His apparatus is shown in Fig. 16. The method of Dieterici was further improved by Maier[4] and Seiferheld.[5] Improvements in the construction of a differential manometer were carried out by Lord Rayleigh,[6] Hering[7] and Mündel.[8] Applying the Rayleigh manometer to the measurement of vapor pressure lowerings, Frazer and Lovelace[9] have described a method of precision which has yielded quite accurate data for solutions of mannite, sucrose, KCl, NaCl, LiCl and HCl over a range of from 20°-30°.[10]

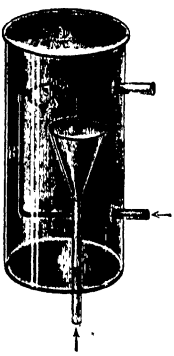

FIG. 16. Apparatus of Dieterici

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[1] *Ann. Physik*, [3] **24**, 523 (1885); **36**, 692 (1889).

[2] *Compt. rend.*, **103**, 1125 (1886); **104**, 976, 1430 (1887); **107**, 442 (1888); *Z. physik. Chem.*, **2**, 353, 372 (1888); *Ann. chim. phys.*, [6] **15**, 297 (1888); **20**, 375 (1890).

[3] *Ann. Physik*, [3] **50**, 47 (1893); **62**, 616 (1897); **67**, 859 (1899).

[4] *Ann. Physik*, [4] **31**, 423 (1906).

[5] Diss. Tübingen, 1911.

[6] *Z. physik. Chem.*, **37**, 713 (1901); *Trans. Roy. Soc.*, **196**, 205 (1901).

[7] *Ann. Physik*, [4] **21**, 319 (1906).

[8] *Z. physik. Chem.*, **85**, 435 (1913).

[9] *J. Am. Chem. Soc.*, **36**, 2439 (1914); *Z. physik. Chem.*, **89**, 155 (1914).

[10] Frazer, Lovelace and Miller, *J. Am. Chem. Soc.*, **38**, 515 (1916); Frazer, Lovelace and Rogers, *ibid.*, **42**, 1793 (1920); Frazer, Lovelace and Sease, *ibid.*, **43**, 102 (1921); Frazer, Lovelace and Bahlke, *ibid.*, **45**, 2930 (1923); H. Parker, Dissertation, Johns Hopkins Univ.

The following description of the apparatus is taken from the original paper of Frazer and Lovelace. The apparatus is shown in Figs. 17, 18 and 19.

"The entire apparatus is built around the Rayleigh manometer, shown in Fig. 17. One side of the manometer communicates with the solvent bulb *H* and the other with the solution bulb *I*. 1, 2, 3, 4, 5, 6 (Fig. 19) are mercury traps which serve as stopcocks. They may be opened or closed by adjusting the position of the mercury reservoirs. The long ones are of barometer height, while the short ones are about 100 mm. high. Since ordinary stopcocks are not employed, the use of lubricant is avoided. The large bulb, *C*, is introduced to increase the capacity of the system and thus facilitate removal of air from solution and solvent. *B* is a phosphorus pentoxide bulb provided with a ground glass joint and mercury seal. *A* is the McLeod gage. All connecting tubes are seven mm. internal diameter.

"After the apparatus was put together all parts of it except the Rayleigh manometer and the phosphorus pentoxide bulb were thoroughly steamed out.

"The bulbs containing solution and solvent are immersed in a water bath, the temperature of which does not vary over periods of several hours more than 0.001°, as read on a Beckmann thermometer. Experience has shown that the Rayleigh manometer is quite sensitive to fluctuations of 0.003° in the bath temperature, if these fluctuations occur over short intervals of time. While it is thus necessary to avoid sensible variations in the temperature of the solution and solvent, no such constancy of temperature is necessary for the other parts of the system.

"In carrying out a complete experiment the following procedure is adopted: The proper amount of carefully cleaned mercury is poured into each of the reservoirs attached to the open ends *M*, *M*, *M* of the apparatus and the entire system exhausted repeatedly to the highest vacuum attainable by the pump. The zero point is then determined, after which, solvent, partially freed from air by boiling, is introduced and the remaining trace of dissolved air removed, as described later. The solution, also partially freed from air, is next introduced, and, after complete removal of dissolved air, the zero point may be redetermined. Finally, the pressure of vapor over the solution is balanced against that of the vapor over the solvent and the scale deflection read. The entire apparatus having been exhausted, trap 5 is closed and the solvent, freed from air as completely as possible by long boiling, is introduced into the bulb. In this operation, the solvent need not come in contact with air and it is, therefore, possible to introduce into the apparatus solvent that is practically air-free. There is, however, in actual practice, always a trace of air to be removed after the solvent is in the bulb. This is accomplished in the following manner: Traps 1, 2 and 4 (Fig. 19) and the McLeod gage are closed, and trap 5 opened and allowed to stay open 24 hours. Trap 5 is then closed and 2 opened. After the absorption of water vapor by the phosphorus pentoxide in *B* is complete, the McLeod gage is opened and the pressure determined. The residual air is pumped out and the process repeated as many times as may be necessary for complete removal of dissolved air. The solvent, having once been freed from air, may remain in the apparatus indefinitely and it is possible at any time to examine its vapor for air. Trap 3 is now closed and 5 opened.

"Fig. 18 shows a device employed for partial removal of air from the solution before it is introduced into the apparatus. The bulb is drawn down at each end to a capillary and enough solution introduced, at the ordinary temperature, to fill the bulb completely at 85°-90°. The lower capillary is then sealed off, the upper end drawn down to a very fine capillary, *A* (about 0.05 mm.), and the whole heated to the temperature at which the solution completely fills the bulb and capillary. The latter is then sealed off and the solution allowed to cool and stand 24 hours in the partial vacuum thus obtained. The tip of the capillary is next broken off and the process repeated. Five repetitions of this operation are sufficient to remove nearly all the air. The solution is then introduced into the bulb *I* without coming in contact with the air and the last traces of dissolved air removed in the manner already

(1921); L. C. Beard, Dissertation, Johns Hopkins Univ. (1922), W. Norris, Dissertation, Johns Hopkins Univ. (1922); R. K. Taylor, Dissertation, Johns Hopkins Univ. (1923); S. S. Negus, Dissertation, Johns Hopkins Univ. (1923), Grollman, unpublished results (1924).

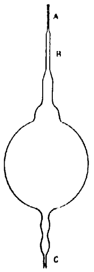

Fig. 18

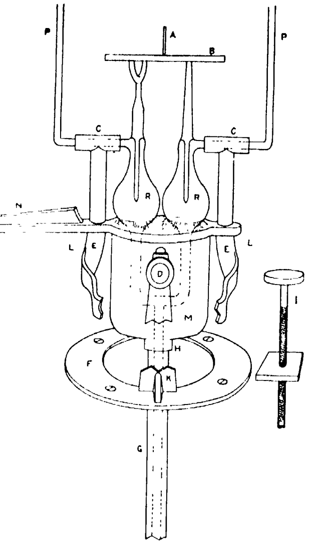

Fig. 17

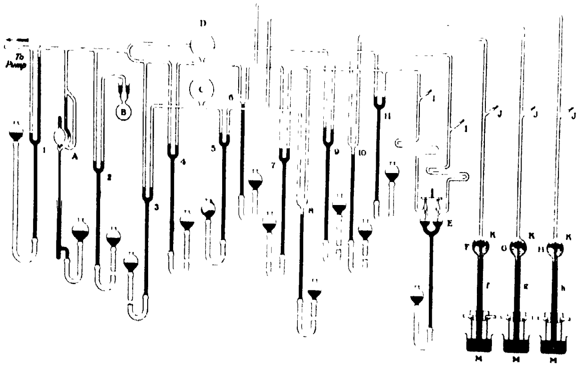

Fig. 19

described for the solvent. The extent to which the solution is concentrated during the process of removal of air after introduction into the bulb *I* may be accurately calculated and never exceeds 0.1 per cent. After the removal of air is complete, trap 4 is closed and 6 opened, and a measurement may now be taken.

"Observations on the Rayleigh manometer during the progress of the removal of air from the solution are very interesting. It is to be remembered that at this stage the vapor pressure of the air-free solvent is balanced against the pressure over the solution, which is equal to the vapor pressure of the solution plus a small air pressure. As long as any air remains in the solution (even the smallest trace), a very long time is necessary for the establishment of equilibrium after the opening of trap 6. The pressure in the solution limb of the manometer, at first very nearly the true vapor pressure of the solution, slowly increases for 24 or 48 hours, depending on how much air remains After equilibrium is attained, the difference in pressure in the two limbs is read in the usual way by noting the scale deflection. To this apparent depression is added the air pressure in the system, subsequently determined by means of the McLeod gage, after absorption of the water vapor by the phosphorus pentoxide. The depression thus obtained agrees very closely, to about 0.001 mm., with the true depression measured later, after complete removal of air"

Results for mannite solutions, obtained by Frazer, Lovelace and Rogers,[1] are given in Table VIII.

TABLE VIII

VAPOR PRESSURE LOWERING OF AQUEOUS MANNITE SOLUTIONS

Grams of Mannite per 1000 G. of Water (in Vacuo)	Conc. in Moles per 1000 G. of Solvent	$p_0 - p_1$ = Vapor Pressure Lowering in Mm Mercury	Lowering Calc. According to Raoult's Law	Difference between Calc. and Obs. Lowerings
17.930	0.0984	0.0307	0.0311	0.0004
36.004	0.1977	0.0614	0.0622	0.0008
53.951	0.2962	0.0922	0.0931	0.0009
71.917	0.3945	0.1227	0.1239	0.0012
89.938	0.4938	0.1536	0.1547	0.0011
108.243	0.5944	0.1860	0.1858	− 0.0002
108.498	0.5958	0.1863	0.1862	− 0.0001
126.283	0.6934	0.2162	0.2164	− 0.0002
144.357	0.7927	0.2178	0.2169	− 0.0009
162.332	0.8913	0.2791	0.2772	− 0.0019
162.485	0.8922	0.2792	0.2775	− 0.0017
180.451	0.9908	0.3096	0.3076	− 0.0020

Another form of differential manometer due to Smits[2] has found application in the accurate measurement of vapor pressure lowerings and is shown in Fig. 20. The lower narrow part of the manometer is filled with aniline (*A*) over which is a layer of water (*B*) which continues into the wider upper portion. This in turn is covered with a layer of oil to prevent any influence of the water vapor. For the mathematical theory of the readings the reader is referred to the original article of Smits or to Jellinek[3]

Dynamic Methods: The dynamic methods of determining vapor pressure lowering are much simpler to carry out experimentally and hence have found wide application, though the results obtained lack somewhat the precision of the best static methods. One can, for example, determine the pressure at which a pure solvent and its solution boil at the same temperature as had been done by A. A. Noyes and C. G. Abbott,[1] H. M. Goodwin and G. K. Burgess,[2] and A. W. C. Menzies.[3] The method of Walker[4] consists in passing a known volume of air through the pure solvent and the solution; by determining the amount of vapor so removed, we can calculate the vapor pressure of the solution in question.

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[1] *J. Am. Chem. Soc.*, **42**, 1801 (1920).

[2] *Z. physik. Chem.*, **39**, 386 (1906).

[3] Lehrbuch der Physikalischen Chemie, vol. 2, p. 759 (Stuttgart, 1915).

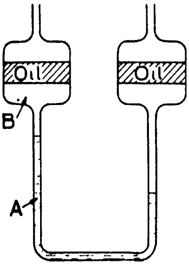

FIG. 20. Manometer of Smits

Excellent results have been obtained by the Earl of Berkeley, E. G. J. Hartley and C. V. Burton,[5] who improved the method by passing the current of air over the liquids in order to avoid change of pressure in the apparatus. These investigators determined the amount of vapor lost by the bulbs containing the solution, while Washburn and Heuse[6] weighed the amount of vapor taken up by absorption in a suitable apparatus. The chief errors in the method are due to the difficulty in accurately measuring the aspirated air and maintaining constant temperatures.[7]

The Experimental Determination of Freezing and Boiling Points: Of all the colligative properties, none lend themselves to experimental determination so easily as freezing and boiling points. The ease and accuracy with which thermometric readings may be made, especially differential readings, as by the Beckmann and platinum resistance thermometers, have made the wide application of such determinations possible. Moreover, since simple relationships are known, whereby the other colligative properties, such as osmotic and vapor pressures, may be calculated, these measurements are used where experimental difficulties make the direct determination of the others difficult or inaccurate. The great limitation in the value of freezing- and boiling-point data, however, lies in the fact that they are limited to a single temperature, and, hence, cannot, without doubtful assumptions, be applied over a range of temperatures.

The earliest determinations of freezing-point lowerings were made by Blagden,[8] who showed the proportionality between freezing-point lowering and concentration. Numerous experiments were later made by Rüdorff[9]

[1] *Z. physik. Chem.*, **23**, 56 (1897).

[2] *Z. physik. Chem.*, **28**, 99 (1899).

[3] *Z. physik. Chem.*, **76**, 231 (1912).

[4] *Z. physik. Chem.*, **2**, 602 (1888).

[5] *Phil. Trans. Roy. Soc.*, **A 209**, 177 (1909), **A 218**, 295 (1919).

[6] *J. Am. Chem. Soc.*, **37**, 309 (1919).

[7] For some very recent determinations of vapor pressure lowerings see Bousfield, *Proc. Roy. Soc.*, **103A**, 429 (1923), and Dieterici, *Ann. Physik*, **70**, 617 (1923).

[8] *Phil. Trans.*, **78**, 277 (1788); Ostwald's Klassiker, No. 56, Leipzig (1894).

[9] *Ann. Physik*, [2] **114**, 63 (1861), **116**, 55 (1862); **122**, 337 (1864), **145**, 599 (1872).

and Coppet,[1] the former of whom developed experimental mechanical details and showed that, from many solutions, the solvent crystallized out in a pure form at the freezing point.

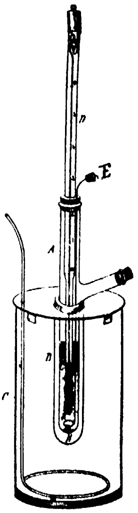

Fig. 21. Beckmann's Apparatus for Freezing-Point Determinations

The extensive work of Raoult[2] led him to his generalization which we have already discussed. Other workers may also be mentioned, Hollemann,[3] Auwers,[4] Fabinyi,[5] Eykmann,[6] Klobukow,[7] but it was not until the work of Beckmann[8] that any experimentally accurate apparatus was devised.

His apparatus, which, due to its simplicity and accuracy, has found wide application, is shown in the accompanying diagram (Fig. 21).

Various refinements in experimental technique have been introduced by the numerous workers who have carried out freezing-point determinations. We may mention the work of Loomis,[9] Raoult,[10] H. C. Jones,[11] Wildermann,[12] P. B. Lewis,[13] Abegg,[14] Hausrath,[15] Ponsot,[16] Roloff,[17] and Richards.[18]

Due to the fact that the formation of a new phase at the freezing point is more regular in its action than at the boiling point, determinations of the former can be carried out with greater accuracy. In both determinations, however, the usual thermometric errors, such as irregularity in bore and sticking of the mercury thread, must be carefully considered and obviated. A source of considerable error is the variable depression of the ice point due to changes in

[1] *Ann. chim. phys.*, [4] **23**, 366 (1871), **25**, 502 (1872), **26**, 98 (1872).

[2] *Ann. chim. phys*, [5] **20**, 217 (1880), **28**, 133 (1883), [6] **2**, 66, 93 (1884), **4**, 401 (1885); **8**, 289, 317 (1886), *Jour. Phys.*, [2] **3**, 16 (1884), **5**, 65 (1886), *Z physik Chem*, **9**, 343 (1892), Cryoscopie, Serie physico-mathematique, No 13, Paris (1911).

[3] *Ber.*, **21**, 860 (1888).

[4] *Ber.*, **21**, 701 (1888).

[5] *Z. physik. Chem.*, **4**, 964 (1889).

[6] *Z. physik. Chem.*, **4**, 497 (1889).

[7] *Z. physik Chem.*, **4**, 10 (1889).

[8] *Z. physik. Chem.*, **2**, 638 (1888).

[9] *Ann. Physik*, [3] **51**, 506 (1894); **57**, 511 (1896), *Z. physik Chem.*, **32**, 581 (1900); **37**, 408 (1901).

[10] *Z. physik. Chem.*, **27**, 622 (1898), *Ann. chim phys*, [7] **16**, 168 (1899).

[11] *Z. physik. Chem.*, **11**, 111, 529 (1893), **12**, 623 (1893), Carnegie Inst. Pub., No. 80, No. 180.

[12] *Z. physik. Chem.*, **15**, 337 (1894), **30**, 510 (1899).

[13] *Z. physik. Chem.*, **15**, 365 (1894).

[14] *Z. physik. Chem.*, **20**, 208 (1896).

[15] *Ann. Physik*, [4] **9**, 542 (1902).

[16] *Ann. chim. phys.*, [7] **10**, 79 (1897).

[17] *Z. physik. Chem.*, **7**, 323 (1891), **22**, 616 (1897).

[18] *Z. physik. Chem.*, **18**, 572 (1895), *J. Am. Chem Soc*, **25**, 291 (1903).

volume of the bulb resulting from molecular changes in the glass with change of temperature. This error is obviated by keeping the thermometer at the temperature of the experiment for a long period and redetermining the ice point after the experiment. In this way its variability may be reduced to 0.0003° C.[1] In the case of precise measurements correction must also be made for pressure variations, both external and internal, which affect the readings. Nernst[2] first showed that in cryoscopic determinations constancy of temperature did not necessarily denote the freezing point, but that a final constant reading might result as well from a balance in the interchange of heat between the freezing mixture and the solution, and the establishment of equilibrium between the liquid and solid phases. Unless this convergence temperature coincides with the true freezing point, errors as high as 20 per cent in the value of the molecular depression could be introduced. Nernst and Abegg indicated, however, how the observed values could be corrected to give the true freezing point. The determination of the concentration at the freezing point is also of fundamental importance and numerous devices have been introduced to make this determination precise.

Of the more recent determinations of freezing points, we may mention the work of Beckmann,[3] Jahn,[4] Bedford,[5] Flügel,[6] Adams,[7] Cernatescu,[8] to which, as well as to the work already cited, reference should be made for a description of the various details necessary for precise determinations. In the method of Adams, whose apparatus is shown in Fig. 22, a rapid and certain equilibrium is brought about by stirring with a large amount of ice; the depression of the freezing point is accurately determined by means of a thermocouple and sensitive potentiometer; and the analysis of the solution is made with a high degree of accuracy by the use of an optical apparatus.

Results obtained by Adams with aqueous mannite solutions are given in Table IX.[9]

Boiling-Point Determinations: The earliest measurements of the raising of the boiling point, due to the addition of a non-volatile solute to a solvent, were made by Faraday,[10] Griffiths,[11] and Legrand,[12] but no accurate work was done until the important work of Raoult[13] and Beckmann.[14]

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[1] Cf. Ostwald, Luther, Drucker, Physico-Chemische Messungen.

[2] Nernst and Abegg, *Z. physik. Chem.*, **15**, 681 (1894). Nernst and Hausrath, *Ann. Physik*, [4] **17**, 1018 (1905).

[3] *Z. physik. Chem.*, **44**, 169 (1903).

[4] *Z. physik. Chem.*, **50**, 129 (1904); **51**, 31 (1907).

[5] *Proc. Roy. Soc.*, **A 83**, 454 (1910).

[6] *Z. physik. Chem.*, **79**, 537 (1912).

[7] *J. Am. Chem. Soc.*, **37**, 481 (1915).

[8] *Ann. Sci. Univ. Jassey*, **10**, 259 (1920).

[9] *J. Am. Chem. Soc.*, **37**, 492 (1915).

[10] *Ann. chim. phys.*, [2] **20**, 324 (1820).

[11] *Ann. Physik*, [2] **2**, 227 (1824).

[12] *Ann. chim. phys.*, [2] **59**, 425 (1835).

[13] *Compt. rend.*, **87**, 167 (1871); **122**, 1175 (1896); *J. Phys.*, [2] **8**, 1 (1889); *Ann. chim. phys.*, [6] **20**, 361 (1890); Tonométrie in Scientia (Carré et Naud, Paris, 1900).

[14] *Z. physik. Chem.*, **3**, 603 (1889); **4**, 532 (1889); **5**, 76 (1890); **6**, 437 (1890); **8**, 223

TABLE IX

FREEZING-POINT DEPRESSIONS OF AQUEOUS MANNITE SOLUTIONS

Concentration Millimols per 1000 Grams H_2O	Freezing-Point Depression (Δ_T) in Degrees (Observed)	Calculated	Diff. Obs.-Calc. (10^{-4} Degrees)
4.02	.0074	.0075	0
8.42	.0157	.0156	1
14.04	.0260	.0261	− 1
28.29	.0525	.0525	0
62.59	.1162	.1162	0

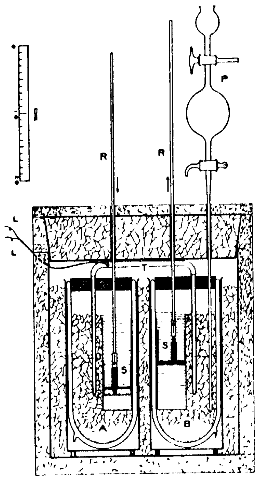

FIG 22. Freezing-Point Apparatus of Adams

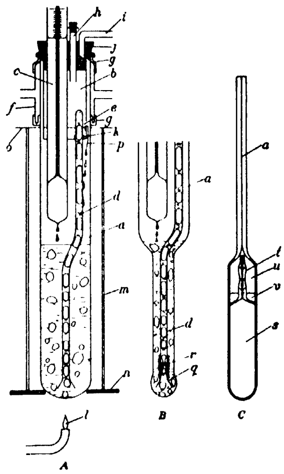

FIG. 23 Boiling-Point Apparatus of Cottrell

Modifications of the Beckmann apparatus have been made which have rendered it a most precise method for physico-chemical measurements.[1] The boiling-point method has certain inherent errors which require special precautions unnecessary in the determination of freezing points. Care must be

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(1891); **15**, 656 (1894), **17**, 106 (1895), **18**, 173 (1895); **21**, 245 (1896); **22**, 609 (1896); **40**, 129 (1902); **44**, 161 (1903), **51**, 329 (1905), **53**, 137 (1905); **58**, 543 (1907); **63**, 177 (1908); **64**, 506 (1908), **78**, 725 (1912), **79**, 565 (1912), **86**, 337 (1914); **88**, 13, 23, 419 (1914).

[1] A. Smits, *Z. physik. Chem*., **33**, 39 (1900); **39**, 404 (1902). Stahler's Handbuch der Arbeitsmethoden in Anorg. Chem., vol. III, pp. 131-164, Leipzig, 1913.

taken to measure the temperature of the solution rather than that of the vapor, which soon cools to its condensation point, giving the temperature of the boiling solvent. This error has been overcome by an ingenious device due to Cottrell[1] who, instead of immersing the thermometer bulb in the liquid, thereby running the risk of error due to superheating, places it in the vapor phase as in the case of a pure liquid, and causes the boiling liquid to pump itself over the thermometer bulb. The apparatus of Cottrell is shown in Fig. 23. The tube *d* serves as a pump and insures the passage of solution in intimate contact with its vapor over the thermometer bulb. The glass sheath, *J*, which is attached to the ground glass stopper, serves to protect the bulb from the condensed vapor. The solute is introduced through the tube *H* and the sample for analysis removed by the application of air pressure at its open end.

The method of heating the solution to be studied is also of primary importance. The early methods in which the heat was applied externally have been replaced by electrical devices first introduced by Bigelow.[2] This method, further improved by Beckmann[3] and Mathews,[4] consists in heating the solution by an electric current which passes through a platinum spiral placed in the solution. The use of this method may be limited by electrolysis which may occur in the solution. Inasmuch as the boiling point is greatly influenced by pressure changes, it is not only necessary to maintain a constant external pressure, by the use of a suitable manostat, but the difference in boiling point of the various layers of the liquid due to hydrostatic pressure of the liquid above it must also be considered. In order to eliminate the influence of the temperature of the environment on that of the liquid under investigation, Beckmann has introduced an apparatus which is surrounded by a mantle in which the pure solvent is maintained at its boiling temperature.

For a description of the various forms of apparatus in use, the reader is referred to the original papers of the numerous investigators, especially the comprehensive work of Beckmann and the authors already cited.[5]

In the method of Sakurai, superheating of the boiling liquid is prevented by passing the vapor of the pure solvent through the pure liquid solution. The vapor condenses in the liquid, which is previously heated almost to its boiling point, the heat thus liberated raising the temperature to its boiling point.

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[1] *J. Am. Chem. Soc.*, **41**, 721 (1919).

[2] *Am. Chem. J.*, **19**, 581 (1897).

[3] *Z. physik. Chem.*, **63**, 187 (1908); **78**, 725 (1912); **88**, 23 (1914).

[4] *Trans. Am. Electrochem. Soc.*, **19**, 81 (1911).

[5] See also Sakurai, *J. Chem. Soc.*, **61**, 989 (1892); Landsberger, *Ber.*, **31**, 461 (1898); Walker and Lumsden, *J. Chem. Soc.*, **73**, 502 (1898); Speyers, *J. Phys. Chem.*, **1**, 766 (1898); Rose-Innes, *J. Chem. Soc.*, **81**, 682 (1902); Burt, *J. Chem. Soc*., **85**, 339 (1904); Turner, *J. Chem. Soc.*, **97**, 1104 (1910); Drucker, *Z. physik. Chem.*, **74**, 612 (1912); Washburn and Read, *J. Am. Chem. Soc.*, **41**, 734 (1919); Reihenberg and Brauer, *Z. physik. Chem.*, **95**, 184, 512 (1920); Menzies and Wright, *J. Am. Chem. Soc.*, **43**, 2314 (1921); Spencer, *J. Am. Chem. Soc.*, **43**, 301 (1921).

THERMODYNAMIC CONSIDERATIONS OF THE LAWS OF DILUTE SOLUTIONS

In our previous considerations we have developed the laws of dilute solutions with special reference to the ultimate particles or molecules which make them up. As in other branches of theoretical chemistry, this point of view, despite the many advantages which it offers, is not essential, but we may develop all our generalizations by thermodynamic considerations, that is, by considering the energy relations involved in the various equilibria with which we have to deal. The study of solutions from the thermodynamic standpoint was first developed by van't Hoff, who was led to their study by his epochal work on the energy relations of chemical reactions and chemical equilibrium.[1] The essential results of van't Hoff's theories have also been developed, without reference to the concept of osmotic pressure, by Planck,[2] who is to be considered, with van't Hoff, as the co-founder of the modern theory of solutions. The general thermodynamic theory has also been expanded chiefly by van der Waals,[3] Van Laar,[4] J. W. Gibbs,[5] G. N Lewis,[6] and E. W. Washburn [7]

van't Hoff's Proof of the Identity of the Gas and Osmotic Pressure Formulæ: As we have already mentioned (p. 236), thermodynamic considerations alone do not allow the development of all the relations of solutions but we must start with some empirical relationship whose accuracy we assume. The identity of the equation $PV = nRT$ for both gaseous and osmotic pressures was first shown by van't Hoff The following demonstration follows more closely that given by Rayleigh [8] In this derivation the applicability of Henry's law will be assumed. This law, which states that the concentration of a gas dissolved in a liquid is proportional to the pressure of the gas at that temperature, has been shown to hold in those cases in which the solute has the same molecular form in the gaseous and dissolved states, and the assumption of its validity may, therefore, be considered as permissible in normal cases.

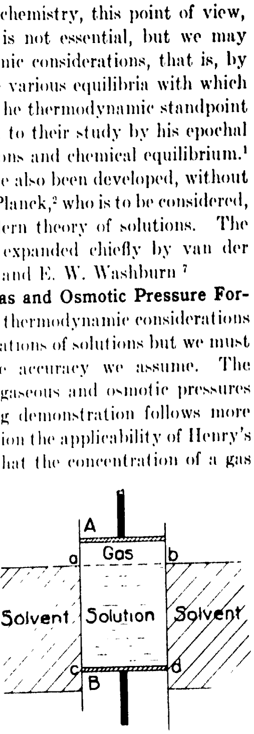

FIG. 21

Let us consider a reversible cyclic process carried out at a constant temperature, T, in which one mole of a dissolved gas is removed from a solution and then restored to its original condition, by use of the imaginary device shown in Fig. 24. A gas, whose pressure is p, in equilibrium with its solution, of osmotic pressure P, is separated from the latter by a semi-permeable membrane ab which only permits the gas to pass through it. Let us assume the vapor pressure of the solvent to be negligible compared with that of the gas. The walls of the cylinder, ac and bd, in which the solution is contained, are permeable to the solvent but do not allow the gas to pass through. The ends of the cylinder are closed by impermeable pistons A and B. Consider the following reversible process:

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[1] *Z. physik. Chem.*, **1**, 481 (1887)

[2] *Ann. Physik*, [3] **32**, 462 (1887) *Z physik. Chem.*, **1**, 577 (1887), **2**, 405 (1888); **6**, 187 (1890). *Ann. Physik*, [4] **10**, 436 (1903).

[3] *Z physik. Chem.*, **5**, 133 (1890).

[4] *Z. physik. Chem.*, **15**, 457 (1899), Sechs Vortrage uber das thermodynamische Potential (Vieweg u. Sohn, Braunschweig, 1906).

[5] *Nature*, **55**, 461 (1897).

[6] *J. Am. Chem. Soc.*, **30**, 668 (1908). Thermodynamics, by Lewis and Randall, McGraw-Hill & Co., N. Y., 1923.

[7] *J. Am. Chem. Soc.*, **32**, 657 (1910).

[8] *Nature*, **55**, 253 (1897).

(1) Let the pistons A and B move upward so that a volume v, equal to the volume occupied by 1 gram-mol. of the gas at pressure p, is transferred through the membrane ab from the solution to the gas. The piston A therefore moves upward through a volume v, while the lower piston B moves through a volume V, equal to the volume of solution in which 1 gram mol. of the gas is dissolved. The solvent corresponding to this volume of solution simultaneously passes through the walls ac and bd. The maximum work done by the system in the reversible movement of the upper piston is pv while that done upon the system by the external surroundings in moving the lower piston is $-PV$, the negative sign indicating work done on the system. Hence the net work done in this stage is $pv - PV$.

(2) We wish now to restore one gram-mol. of the gas at a pressure p to the solution by a reversible and isothermal path so as to obtain the maximum work. Consider a volume v of the gas at pressure p, separated from the system. Let this gas expand isothermally and reversibly to practically infinite volume, so that the maximum work done in this process is

$$\int_{v_0}^{v_\infty} pdv = \int_{v_0}^{v_\infty} \frac{RT}{v}dv = RT\int_{v_0}^{v_\infty}\frac{dv}{v} = RTln\frac{v_\infty}{v_0}\cdot$$

If the gas is now brought into contact with a volume V of solvent, it will dissolve infinitely slowly, since it is infinitely dilute, and the process will, therefore, be reversible. If the gas is gradually compressed by a frictionless piston, it will dissolve and the work done on the system by this process will be

$$-\int_{v_0}^{v_\infty} p_1dv_1.$$

To evaluate this integral we must obtain a relation between p_1 and v_1. They are not related by the equation $p_1v_1 = RT$ since at any stage of the solution process we no longer are dealing with one mole, some of the gas having already dissolved. When one mole of the gas has dissolved, the pressure of the piston is p so that, if we assume the validity of Henry's law regarding the proportionality being the amount of gas dissolved and its pressure, $\frac{p_1}{p}$ mole of gas will dissolve at the pressure p_1, leaving $1 - \frac{p_1}{p}$ undissolved. Applying the perfect gas equation to this amount of gas, we have at any stage

$$p_1v_1 = \left(1 - \frac{p_1}{p}\right)RT,$$

and substituting for p its value, $\frac{RT}{v}$, we finally obtain

$$p_1 = \frac{RT}{v + v_1}$$

as our desired relation with which we may now derive the value of the integral

$$-\int_{v_0}^{v_\infty} p_1dv_1 = -\int_{v_0}^{v_\infty} RT\frac{dv_1}{v_1 + v} = -RT\ln\frac{v_\infty + v}{v}.$$

Since v is negligible compared to v_∞, we can write the last expression as

$$-RT\ln\frac{v_\infty}{v}.$$

If now we return this volume of solution to the original solution, which process involves no work, we have our original system and hence the sum of the work terms done in this reversible and isothermal cycle must be equal to zero. That is,

$$pv - PV + RT\ln\frac{v_\infty}{v} - RT\ln\frac{v_\infty}{v} = 0$$

or

$$pv = PV.$$

But, by the perfect gas law, $pv = RT$. Hence, also,

$$PV = RT,$$

which is our desired relationship.

Relation between Osmotic Pressure and Vapor Pressure Lowering of a Solution: The vapor space above a solution which contains but one volatile constituent may be regarded as an ideal semi-permeable membrane permitting the removal of this constituent only. Let us imagine an apparatus as in Fig. 25, which consists of a cylinder fitted above with a piston which permits the passage of only the vapor of the solvent and at the bottom with a membrane which permits the passage of only the liquid solvent. Intervening between the solution and piston is a gas (helium, for example) which dissolves but slightly in the liquid and serves to transmit the pressure exerted by the piston. If a pressure p is put on the system by the piston which is equal to

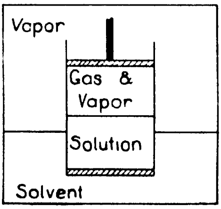

FIG. 25

the osmotic pressure P of the solution, then equilibrium must exist at both the upper and lower membranes, otherwise a continuous circulation of the solvent would occur through the cell. Therefore, the partial pressure of the solvent in the gas space beneath the upper piston must be equal to the vapor pressure of the pure solvent outside and the osmotic pressure may be defined as the excess pressure which must be put on a solution in order to make the vapor pressure from the solution equal to that of the pure solvent at the same temperature. The effect of mechanical pressure on the vapor pressure of a liquid was first shown by Thomson and is expressed in the following equation:

$$\frac{dp_0}{dP} = \frac{V_0}{v},$$

where P is the applied pressure, V_0 is the molal volume of the liquid and v its molal volume in the vapor state.

For the relation between osmotic pressure and vapor pressure at equilibrium, we have from the above relation

$$\frac{dp}{dP} = -\frac{V_0}{v}.$$

Here, V_0 is the molal volume of the solvent in the solution. Then, since

$$v = \frac{RT}{p},$$

$$dP = -\frac{RT}{V_0} \cdot \frac{dp}{p}.$$

But since

$$\frac{dp}{p} = -\frac{dx}{1 - x},$$

$$dP = \frac{RT}{V_0} \frac{dx}{1 - x},$$

the integral of which gives

$$P = \frac{RT}{V_0}\left[-ln(1 - x)\right],$$

which on expansion becomes

$$P = \frac{RT}{V_0}(x + \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 + \cdots).^1$$

In the case of dilute solutions, where x is small, the above equation reduces to $PV_0 = xRT$. The same relation may be shown in the following manner:

The osmotic pressure of a solution is only a manifestation of the lack of equilibrium between solution and pure solvent which also manifests itself in

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[1] See Findlay, Osmotic Pressure, page 61.

the vapor phase by a difference in vapor pressure of the two. By the following isothermal and reversible cycle we wish to derive a relation between the osmotic pressure and lowering of the vapor pressure due to the presence of a non-volatile solute. Let us imagine a cylinder, as shown in the accompanying diagram (Fig. 26), containing a solution in contact with its vapor at a pressure p. The cylinder is closed at the bottom by a piston ab acting as a semipermeable membrane by means of which the pure solvent can be removed osmotically from the solution. Let p_0 be the vapor pressure of the pure solvent and P the osmotic pressure of the solution.

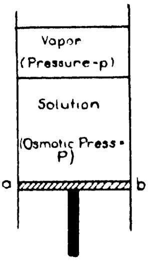

FIG. 26

(1) By means of the piston ab, which, acting as a semi-permeable membrane, allows the passage of solvent but is impermeable to the solute, let us remove osmotically and reversibly the volume of solvent dv. The work done by this process is $-Pdv$, the negative sign indicating work done on the system. (2) Let us allow this amount of solvent to be distilled isothermally and reversibly and expanded to yield its vapor at a pressure, p. By this reversible expansion at the temperature T, we gain an amount of work for one mole equal to

$$RTln\frac{p_0}{p}\cdot$$

If the amount contained in the volume dv was dx moles, the work done by the system will be

$$dxRTln\frac{p_0}{p}\cdot$$

(3) If this vapor is now condensed at the temperature T and pressure p, in contact with the solution, the heat expended by the condensation will be equal to that gained by the system in the evaporation considered in (2) and hence these two effects cancel one another and need not be evaluated.

Our system has now returned to its original state, and since the cyclic process has been carried out isothermally and reversibly, the net work must be zero, that is,

$$-Pdv + dxRTln\frac{p_0}{p} = 0.$$

If M is the molecular weight of the solvent in the vapor state, $\frac{Mdx}{dv}$ will be the density of the liquid solvent which we shall denote by ρ. Substituting in the above equation for $\frac{dx}{dv}$ its value $\frac{\rho}{M}$, we obtain

$$ln\frac{p_0}{p} = \frac{PM}{\rho RT},$$

which is the required relation between the osmotic pressure of a solution, P, and the lowering of the vapor pressure of the pure solvent $p_0 - p$. The relation between vapor pressure lowering and osmotic pressure, as well as the variation of vapor pressure with hydrostatic pressure, has also been developed by J. J. Thomson[1] to which the reader is referred.

Raoult's Equation for Vapor Pressure Lowering: In the case of a dilute solution to which van't Hoff's law of osmotic pressure applies,

$$P = cRT,$$

where c is the molar concentration of the solution. We may therefore write

$$ln\frac{p_0}{p} = \frac{cM}{\rho}$$

or

$$ln\frac{p_0}{p} \propto c,$$

which is the thermodynamically accurate form of Raoult's law. If the solution is very dilute, i.e., $p_0 - p$ is very small, we may write

$$ln\frac{p_0}{p} = ln\left(1 + \frac{p_0 - p}{p}\right)$$

and, since the logarithm of one plus a very small number equals the number (McLaurin's theorem), we may write $\frac{p_0 - p}{p_0}$ for $ln\frac{p_0}{p}$. The term $\frac{M}{\rho}$ in the above equation is equal to V_0, the volume of one mole of the solvent which in a dilute solution can be set equal to V_1, the volume of one mole of the solution. Let us also write c as $\frac{N}{V}$, where N is the number of moles of solute contained in the volume V of solution. Substituting these values in the original equation, we obtain

$$\frac{p_0 - p}{p_0} = \frac{NV_0}{V} = \frac{N}{N_0},$$

where N_0 is the number of moles of solvent in which N moles of solute are dissolved. This is the simple equation of Raoult which we have already derived in a previous section on purely kinetic grounds.

Osmotic Pressure Formula for Higher Concentrations: The simple form of the van't Hoff equation $P = cRT$, though applicable to very dilute solutions, is, nevertheless, only a limiting form of a more general equation which we will now derive from the above relationship between osmotic and vapor pressures:

$$ln\frac{p_0}{p} = \frac{PM}{\rho RT}.$$

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[1] Applications of Dynamics to Physics and Chemistry.

If V_0 is the molal volume of the solvent, we may substitute it for $\frac{M}{\rho}$ in the above equation and write it

$$P = \frac{RT}{V_0} \ln \frac{p_0}{p},$$

which is an exact expression even at large concentrations, provided the perfect gas laws apply to the vapor and the effect of pressure on the molal volume V_0 be negligible. If we wish to express osmotic pressure in terms of the concentration of the solute, we must apply Raoult's law, i.e., substitute for $\frac{p_0}{p}$ its value obtained from the relation

$$p = p_0(1 - x),$$

where x is the molar fraction of the solute. Our equation then becomes

$$P = \frac{RT}{V_0} \ln \left(\frac{1}{1 - x} \right) = \frac{RT}{V_0} [- \ln(1 - x)].$$

On expanding the term $\ln(1 - x)$, the last equation becomes

$$P = \frac{RT}{V_0} (x + \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 \cdots),^1$$

which is the accurate form of the equation required. In the case of very dilute solutions, x is very small and hence its higher powers may be neglected, so that the above equation may be written

$$PV_0 = xRT.$$

In the case of a solution in which 1 mole of solute is contained in a volume V of solution, this may be written $PV = RT$, which is the simple form of the van't Hoff equation.

Relation between Osmotic Pressure and Boiling-Point Elevation: A relation similar to those derived above will now be derived for the osmotic pressure and boiling-point elevation of a solution. Let us assume (Fig. 27) that we have a solution enclosed by means of a frictionless semipermeable membrane ab, which acts as a piston, allowing solvent to be removed osmotically and reversibly. The solution whose osmotic pressure is P is at its boiling temperature, $T + dT$, where T is the boiling point of the pure solvent and dT the boiling-point elevation.

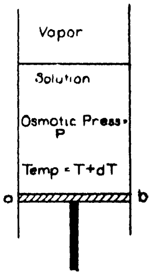

FIG. 27

(1) By means of the piston ab remove a volume dv, whose weight is dx grams of the solvent whereby the work $- Pdv$ is involved.

---

[1] Cf. Findlay, Osmotic Pressure, Longmans Green & Co., 1919.

(2) Allow this volume of solvent at temp. $T + dT$ to be evaporated isothermally, thus requiring an amount of heat equal to Ldx, where L is latent heat of evaporation per gram of solvent.

(3) The vapor and the solution are now cooled to the temperature T.

(4) At this temperature place the vapor in contact with the solution again, allowing it to condense and thereby giving an amount of heat L_1dx, where L_1 is the latent heat at temperature T.

(5) Raise the temperature of the system adiabatically to the original temperature $T + dT$. The work in this process is equal and opposite in sign to the work in (3) and hence neither need be evaluated.

Since we have carried out a reversible cyclic process, the algebraic sum of all the work terms involved can be equated to zero, i.e.,

$$- Pdv + Ldx - L_1dx = 0,$$

$$+ Pdv = Ldx - L_1dx.$$

Ldx is the heat absorbed by the system at temperature $T + dT$, and L_1dx that given up at the lower temperature T. We can, therefore, apply the expression of the second law

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1},$$

where Q_1 is the heat absorbed at temperature T_1 and Q_2 that given up at T_2, so that substituting for $Ldx - L_1dx$ its value

$$\frac{T + dT - T}{T + dT} Ldx,$$

we obtain

$$Pdv = \frac{dT}{T + dT} Ldx,$$

and writing $\frac{dx}{dv} = \rho$, the density of the solvent, we obtain

$$P = \frac{L\rho dT}{T_1},$$

where T_1 is the boiling point of the solution, which is our required relationship between the osmotic pressure, P, and the boiling-point elevation dT.

Since the solution is dilute, we can substitute for P its value in the equation $P = cRT$, which for the temperature T_1 becomes $P = cRT_1$, and obtain

$$dT = \frac{RT_1^2c}{L\rho},$$

which is the thermodynamically accurate form for the relation between boiling-point rise and concentration.

Osmotic Pressure and Freezing-Point Lowering: By considering a similar cyclical process in which an amount of solvent is removed from a solution at the freezing point of the pure solvent, T_0, allowed to freeze, cooling the entire system to the freezing point of the solution, $T_0 - dT$, returning the solid solvent previously removed back to the solution, by allowing it to melt, and finally restoring the whole system adiabatically to its original temperature, T_0, we can derive a similar relation between the freezing-point lowering and osmotic pressure of a solution, viz.:

$$P = \frac{L\rho dT}{T_0},$$

where L is the latent heat of fusion per gram of solvent, T_0 its freezing point, ρ its density, P the osmotic pressure and dT the freezing-point lowering. By a substitution for the value of P, as was made in the case of the boiling-point relationship, we obtain the equation connecting the freezing point and concentration of a solution

$$dT = \frac{RT_0^2c}{L\rho},$$

where c is the concentration of the solute.

KINETIC THEORIES OF OSMOTIC PRESSURE

As we have already seen (page 244), van't Hoff[1] first showed the analogy between osmotic and gas pressure by showing the applicability of the same equation

$$PV = RT$$

for both cases. In this equation, P is the osmotic pressure, when 1 mole of solute is contained in volume V of solution and is also the gas pressure that would be produced if this same amount of solute were present as a gas in the volume V. Just as the applicability of the perfect gas equation has been extended by the introduction of various correction factors, so numerous modifications of the simple osmotic pressure formula have been suggested which claim better concordance with experimental results and applicability over a wider range of concentrations. These relationships, being based on a kinetic conception of osmotic pressure, are usually referred to as kinetic theories of osmotic pressure.

It was found in the early work[2] on direct measurements of osmotic pressure that results more concordant with experiment are obtained if instead of expressing V in terms of the volume of solution we express it in terms of the volume of solvent (water) at its maximum density. This variation really amounts to correcting for the volume occupied by the dissolved substance, analogously to the correction made in the case of gaseous pressures for the volume occupied by the molecules themselves. A comparison of values obtained by these two methods is given in Table X.

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[1] *Z. physik. Chem.*, **1**, 481 (1887).

[2] Morse and Frazer, *Am. Chem. J.*, **34**, 28 (1905); **38**, 212 (1907).

TABLE X

OSMOTIC PRESSURE OF AQUEOUS SUCROSE SOLUTIONS AT 20° FROM MEASUREMENTS OF MORSE AND FRAZER

Weight Normal Concentration (Moles Sugar per 1000 Grams of Water)	Volume Normal Concentration (Moles Sugar per Liter of Solution)	Osmotic Pressure Calculated According to		Osmotic Pressure Observed
		Morse and Frazer	van't Hoff	
0.1	0.098	2.40	2.36	2.59
0.2	0.192	4.81	4.63	5.06
0.3	0.282	7.21	6.80	7.61
0.4	0.370	9.62	8.90	10.14
0.5	0.453	12.00	10.9	12.75
0.6	0.533	14.4	12.8	15.39
0.7	0.610	16.8	14.7	18.13
0.8	0.685	19.2	16.5	20.91
0.9	0.757	21.6	18.2	23.72
1.0	0.825	24.0	19.8	26.64

As will be seen by comparing the last three columns, much better agreement between the calculated and observed values is obtained by using weight normal concentrations.

In other words we should, in calculating osmotic pressures, use the formula

$$P = C'RT,$$

where C' is the so-called Raoult concentration referred to one liter of solvent, instead of the equation $P = cRT$ in which the concentration, c, is expressed as volume concentration.

Sackur [1] and Porter [2] have similarly shown that by the use of the formula

$$P(V - b) = RT,$$

in which V represents the volume of solution in which one mole of solute is dissolved and b is a factor correcting for the volume occupied by the solute, we obtain results in agreement with experiment, as is seen by the data of Table XI.

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[1] *Z. physik. Chem.*, **70**, 477 (1910).

[2] *Trans. Farad. Soc.*, **13**, 128 (1917).

TABLE XI

Comparison of Osmotic Pressures of Aqueous Sucrose Solutions at 0° Calculated by Sackur, with Measurements of Berkeley and Hartley

PV Observed	V	P in Atmospheres	PV Calculated
26.7	1.910	14	26.6
30.7	1.144	26.9	30.5
36.0	0.819	44.0	35.5
43.0	0.637	67.5	42.6
52.6	0.522	100.8	52.6
61.1	0.458	133.7	62.4

PV (calculated) in the above table is derived on the basis $b = 0.30$, so that PV (calculated) $= RT + bP = 22.4 + 0.30P$. The factor, b, however, is not a constant but varies with temperature and concentration, which variation is attributed to changes in hydration with a concomitant change in the volume occupied by the solute. This simple equation, however, fails to correct for the mutual attractions between solute and solvent molecules and hence its agreement with experimental results, in the cases to which it has been applied, can only be attributed to a fortuitous balancing of these effects. Moreover, as Schay[1] has pointed out, the equation of Sackur,

$$P = \frac{RTc}{1 - bc},$$

expressing V in terms of concentration, merely involves a correction in the denominator, and hence we may write it as

$$P = RTc(1 + bc),$$

which being a quadratic in c would be expected to give values in comparatively close agreement with experiment.

A great number of more complicated equations have been suggested by Bredig,[2] A. A. Noyes,[3] van der Waals,[4] Boltzmann,[5] Lorentz,[6] Berkeley and Hartley,[7] Callendar,[8] Fouard,[9] Jaeger,[10] Ehrenfest,[11] Jellinek,[12] and others, in which an analogy to the van der Waals' equation for gases has been sought that would correct for both volume and attraction factors. These equations are, however, very unsatisfactory, due to the possible multiplicity of forms that they may take, and the difficulties in ascribing any definite meaning to the empirical constants which they contain and which usually vary considerably.

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[1] *Z. physik. Chem.*, **106**, 378 (1923).

[2] *Z. physik. Chem.*, **4**, 444 (1889).

[3] *Z. physik. Chem.*, **5**, 53 (1890).

[4] *Z. physik. Chem.*, **5**, 133 (1890).

[5] *Z. physik. Chem.*, **6**, 474 (1890).

[6] *Z. physik. Chem.*, **7**, 36 (1891).

[7] *Proc. Roy. Soc.*, **A 79**, 125 (1907).

[8] *Proc. Roy. Soc.*, **A 80**, 466 (1908); *Z. physik. Chem.*, **63**, 641 (1908).

[9] *Bull. Soc. Chim.*, [4] **13**, 784 (1913).

[10] *Ann. Physik*, [4] **41**, 854 (1913).

[11] *Proc. Akad. Weten. Amst.*, **17**, 1241 (1915); *Ann. Physik*, **48**, 369 (1915).

[12] *Z. physik. Chem.*, **92**, 169 (1918).

O. Stern[1] has deduced an expression based on van der Waals' equation in which he considers a solution in which there is no molecular complex formation as a liquid mixture of two molecular species. He therefore expresses the partial osmotic pressures of the constituents individually by use of a relationship deviating somewhat from the original equation of van der Waals and derived[2] from the virial theorem. By correcting for the mutual attraction between solute and solvent Stern finally deduces the expression

$$P = \frac{RT}{V} + \frac{RT}{V^2}[b_1 - b_{12}(x_0 - x)] - \frac{1}{V^2}[a_1 - a_{12}(x_0 - X)].$$

Adverse criticism of this equation by van Laar[3] as regards the legitimacy of using van der Waals' equation as a basis for a general theory of solutions has been met by Jellinek,[4] who points out that the equation is applicable if we assume the additivity of the volumes of solvent and solute and of the volume correction factor b.

Recently, Schay,[5] by considering the observed osmotic pressure as resulting not from the bombardment of the dissolved particles on the membrane but rather as representing the difference in pressures of the solvent in the pure condition and in the solution, has extended the equation of Stern. This difference in pressures of solvent and solution he visualizes as being occasioned by the fact that the collisions per given area of the membrane due to the solvent particles in the solution are less frequent than those of the pure solvent over the same area, due to the relative sparsity of the former compared to the latter. This difference in the number of collisions on both sides of the membrane also accounts for the diffusion of solvent from the region of more frequent bombardment (solvent) into the solution. The final equations derived, however, despite their theoretical interest, offer no superiority over the simpler Sackur or Raoult formulæ in so far as practical application is concerned.

The above considerations have been limited to a discussion of solutions in which dissociation or complex formation is absent. The application of the kinetic theory to electrolytes has been less extended, due to the complexity involved in introducing factors which should express the variation of the electrical effects of the ions as a function of concentration.

P. Debye,[6] beginning with the assumptions that:

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[1] *Z. physik. Chem.*, **81**, 441 (1913).

[2] Cf. Boltzmann, Gastheorie, II, p. 139.

[3] *Z. physik. Chem.*, **82**, 223 (1913).

[4] *Z. physik. Chem.*, **92**, 169 (1918).

[5] *Loc. cit.*

[6] *Rec. trav. chim.*, **42**, 597 (1923).

(1) Strong electrolytes are completely dissociated at all concentrations,
(2) The observed values in limiting laws (at zero concentration) may be attributed to mutual electric forces between the ions themselves and the molecules of the solvent,

has developed a mathematical theory of osmotic pressure based solely on kinetic grounds. By applying a consideration of the thermodynamic potential to the reasoning which had previously led him to deduce a relation for the freezing points of solutions, Debye[1] develops the expression

$$P = \gamma nkT + \varphi(n),$$

in which γ is the number of ions into which each molecule dissociates, n the number of molecules per cubic centimeter, k the Boltzmann constant $= 1.346 \times 10^{-16}$ erg, and T the absolute temperature. This expression is seen to give the osmotic pressure in the form of the classic formula corrected by an additive term, due to the electrostatic forces between the ions, which is a function of concentration. This function is further developed but its lengthy mathematical treatment need not be considered here.[2]

Despite the plausibility and numerous applications of the kinetic theory of osmotic pressure, no generally satisfactory relationship has as yet been derived. This failure is probably due not to any fundamental fault in the basic reasoning of the theory, but is rather to be attributed to the complexity of the forces involved in the phenomenon, which, in our present state of knowledge, do not allow exact formulation.

THE MECHANISM OF OSMOTIC PRESSURE[3]

Theories Regarding the Nature of Semi-permeability: When one substance is dissolved in another, the solvent in the solution thus formed has a free energy value, thermodynamic potential, or activity, different from that of the pure solvent. It is the tendency towards equalization of this difference and the attainment of an equilibrium condition which manifests itself in the production of an osmotic pressure when the two substances are separated by a semi-permeable membrane. This statement, however, tells us nothing of the mechanical details nor does it give us a view of the actual mechanism whereby this pressure is produced.

Experimental determinations of osmotic pressure have always been carried out with semi-permeable membranes. Numerous explanations have therefore been offered regarding the mechanism of this semi-permeability, but they all suffer from the fallacy that they are based on particular cases which they may satisfactorily explain, but lack any general application. We may thus mention

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[1] Debye and Huckel, *Physik. Z.*, **24**, 185 (1923).

[2] See Chapter XII.

[3] For a more detailed discussion of this subject, the reader is referred to the monograph on Osmotic Pressure by Alexander Findlay (Longmans, Green & Co., 1919), p. 94; the Symposium on the same subject in the *Transactions of the Faraday Society*, vol. 13, p. 133, Jellinek, *Physikalische Chemie*, vol. I.

(1) the theory of M. Traube[1] *who considered the action of the membrane as being that of an atomic sieve, allowing only molecules of certain dimensions to pass but preventing the passage of larger particles of solute;*

(2) the theory of capillarity in which the membrane plays the part of a series of fine capillary tubes;[2]

(3) the chemical theory where actual combination of the membrane and solvent take place;[3]

(4) the theory of preferential solubility.[4]

It is probable that no single mechanism will explain all cases, varied mechanisms being possible, depending on the type of membrane used, whether colloidal, as $Cu_2Fe(CN)_6$, animal, as parchment, inert, as glazed porcelain plates, etc. In most cases it is probably a combination of causes, the resultant of which brings about the observed action. The nature of the mechanism of semipermeability does not, however, enter into the theoretical considerations of osmotic pressure and, hence, is of no fundamental importance in such considerations.

The Nature of Osmotic Pressure: Regarding the nature of osmotic pressure, widely divergent views have been expressed. As a result of the analogy which has been shown to exist between gaseous and osmotic pressures, the view has suggested itself that osmotic pressure is due to the bombardment of the membrane by the solute and hence is a force whose nature depends on the dissolved substances. The objection to this kinetic theory, on the grounds that if this were the true origin of the phenomenon we would expect a flow of solvent from the solution, instead of into it, is irrelevant if we regard the case as analogous to the experiment of Ramsay cited previously (page 245). The number of collisions by solvent particles on a given area of the membrane per unit time will be less on the side of the solution than on the solvent side, and, hence, there will be a flow of solvent into the solution until the number of these collisions on both sides of the membrane is equalized, or rather until the flow of solvent through the membrane is the same in both directions.

The other prominent theory of the nature of osmotic pressure considers the solvent as playing the chief rôle in osmosis. This hydrostatic theory, as it is called, attributes osmotic pressure to the entrance of solvent into the solution as a result of an attraction of solvent for solute. This entrance of solvent into the solution has been attributed to various factors. It has been explained[5] as due to the difference in surface tension of solvent and solution. Armstrong[6] has developed a theory according to which osmotic pressure in aqueous solutions results from hydrodynamic conditions, that is, the osmotic pressure of an aqueous solution is the hydraulic pressure exercised by the extra molecules of hydrone attracted into it by the complexes formed by the solute and hydrone. This theory is only a special case of the general idea that osmotic phenomena are due to an attraction between solute and solvent, resulting in the formation of definite and stable compounds such as hydrates in the case of aqueous solutions. This view has been championed by S. U. Pickering[1] who found that if a solution of propyl alcohol and water in a porous cup be surrounded by either the pure alcohol or water, there is always an osmosis of the pure liquid into the cup. This woulld indicate that the porous cup is not impermeable to any one constituent of the solution but rather to the hydrate formed in solution.

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[1] Traube, *Archiv. für Anat. Physiol. Med.* (1867), p. 87.

[2] Bigelow, *J. Am. Chem. Soc.*, **29**, 1675 (1907).

[3] Armstrong, *Proc. Roy. Soc.*, **B 81**, 94 (1909); **A 103**, 610 (1923); *Compt. rend.*, **177**, 257 (1923).

[4] L'Hermite, *Ann. chim. phys.*, [3] **43**, 420 (1855).

[5] Traube, *Ber.*, **17**, 2294 (1884); *Phil. Mag.*, [6] **8**, 704 (1904). Moore, *Phil. Mag.*, [5] **38**, 279 (1894).

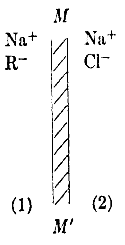
[6] *Proc. Roy. Soc.*, **A 103**, 610 (1923); *Compt. rend.*, **176**, 1892 (1923). Gellet, *Compt. rend.*, **177**, 257 (1923).

None of the theories advanced thus far seems to be entirely satisfactory. A satisfactory explanation of the nature of osmosis will most probably have to await a more thorough knowledge of the nature of solution, the dynamical properties of which are still insufficiently known.

DONNAN'S MEMBRANE EQUILIBRIUM

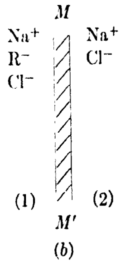
One might expect "a priori" that a substance capable of diffusing through a membrane should distribute itself equally on both sides of this membrane independently of other substances that might be present. The presence, however, of another substance whose molecule is non-diffusible and which can dissociate into a diffusible and non-diffusible ion will cause an unequal distribution of an electrolyte towards whose molecule and ions the membrane is permeable. The theory advanced by F. G. Donnan[2] in 1910 to cover this distribution of ions has found a far-reaching and successful application in the fields of colloidal and physiological chemistry where we often meet the conditions bringing about this phenomenon.

We can best develop this theory by considering a specific case as has been done by Donnan in his original article.[3] Let us consider a membrane (MM^-,



(a)

FIG. 28a



(b)

FIG. 28b

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[1] *Ber.*, **24**, 3639 (1891); *Nature*, **55**, 515 (1900).

[2] Address to London Physiological Society, Dec., 1910.

[3] Donnan, *Z. Elektrochem.*, **17**, 572 (1911). Lewis, System of Physical Chemistry, Longmans, Green & Co. (1919), vol. 2, p. 275.

Fig. 28*a*) impermeable both to the molecule of a salt NaR (e.g., the sodium salt of congo red) and the anion R^- which it gives on dissociation, permeable to the cation, Na^+, as well as to the molecules or ions of other salts. This impermeability of the membrane towards any species of dissolved substance may be considered merely as a result of the small diffusion velocity of the species in question through the membrane due to its size, which permits us to neglect it compared with the diffusion velocities of the other substances in question. The true nature of this impermeability need not be considered. If, now, we imagine a solution of the salt NaR to be on one side of the membrane, (1), and a solution of diffusible NaCl to be on the other, (2), the latter will diffuse through the membrane to side (1) until an equilibrium is reached as represented by the arrangement (Fig. 28*b*). This equilibrium is characterized by the condition that the maximum work obtained in an isothermal and reversible transference of an infinitesimal amount of sodium ions, δn, in one direction is equal to that expended in a similar transportation of δn chlorine ions in the same direction. The algebraic sum of the total work done (i.e., the decrease in free energy) must, therefore, be equal to zero. The work obtained in the transport of δn moles of Na^+ from the side (1) where its concentration is $[Na^+]_1$ to side (2) where it is $[Na^+]_2$ will be equal to

$$\delta nRTln\frac{[Na^+]_2}{[Na^+]_1}$$

and, similarly, for the chlorine ion this work is

$$\delta nRTln\frac{[Cl^-]_2}{[Cl^-]_1}.$$

But, at equilibrium, as stated above,

$$\delta nRTln\frac{[Na^+]_2}{[Na^+]_1}+\delta nRTln\frac{[Cl^-]_2}{[Cl^-]_1}=0, \qquad [1]$$

whence we derive the relationship

$$[Na^+]_2.[Cl^-]_2=[Na^+]_1.[Cl^-]_1, \qquad [2]$$

i.e., the products of the permeable anions and cations on each side of the membrane are equal. No consideration need be taken, in the above derivation of the work necessary for this virtual change in the system, of any potential difference between [1] and [2] inasmuch as equal quantities of both positive and negative electricity have been transferred. The above quantities derived for the work terms in equation [1] assume the applicability of van't Hoff's osmotic pressure law which assumption is valid, since we are limiting ourselves to a consideration of dilute solutions.

We can derive a similar expression for the equilibrium conditions with respect to the undissociated NaCl by considering an infinitesimal, isothermal, reversible transference of δn moles from [2] to [1]. Assuming, here also, the applicability of the van't Hoff generalization, we have

$$\delta nRTln\frac{[\mathrm{NaCl}]_2}{[\mathrm{NaCl}]_1} = 0 \qquad [3]$$

or

$$[\mathrm{NaCl}]_1 = [\mathrm{NaCl}]_2, \qquad [4]$$

i.e., the concentration of the undissociated molecules to which the membrane is permeable is the same on both sides of the membrane. Combination of equations [2] and [4] leads to the expression of the mass action law for ionized substances

$$\frac{[\mathrm{Na}^+].[\mathrm{Cl}^-]}{[\mathrm{NaCl}]} = \text{Constant},$$

which we know to be non-applicable, assuming the accuracy of the values for the degree of dissociation as derived from conductivity measurements. The difficulty need not disturb us, however, as it rests on an assumption which we now know to be inexact.

Returning to equation [2], it is evident that to obtain electroneutrality in the solution, $[\mathrm{Na}^+]_1$ must equal $[\mathrm{R}^-] + [\mathrm{Cl}^-]_1$ and $[\mathrm{Na}^+]_2 = [\mathrm{Cl}^-]_2$, and hence we can write equation [2] as

$$[\mathrm{Na}^+]_1.[\mathrm{Cl}^-]_1 = [\mathrm{Na}^+]_2^2 = [\mathrm{Cl}^-]_2^2,$$

whence it follows that neither $[\mathrm{Na}^+]_1 = [\mathrm{Na}^+]_2$ nor does $[\mathrm{Cl}^-]_1 = [\mathrm{Cl}^-]_2$, since $[\mathrm{Na}^+]_1 \neq [\mathrm{Cl}^-]_1$, which follows from the above statement

$$[\mathrm{Na}^+]_1 = [\mathrm{R}^-] + [\mathrm{Cl}^-]_1.$$

To obtain a better and more quantitative statement of the above conditions let us assume

(1) Complete dissociation of NaR and NaCl.

(2) Equal volumes of liquid on both sides of the membrane, which we may represent diagrammatically in Fig. 29 thus:

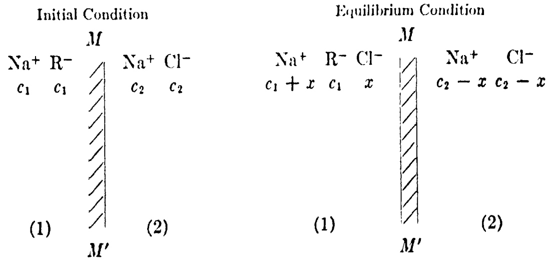
Initial Condition
M
Na^+ R^-
c_1 c_1
Na^+ Cl^-
c_2 c_2
(1)
M'
(2)
Equilibrium Condition
M
Na^+ R^- Cl^-
$c_1 + x$ c_1 x
Na^+ Cl^-
$c_2 - x$ $c_2 - x$
(1)
M'
(2)

FIG. 29

in which the molar ionic concentrations of the various constituents are represented by the algebraic symbols, and x represents the concentration of Na^+ and Cl^- which have diffused through the membrane.

If we now substitute these symbols for the concentrations, in the equation

$$[Na^+]_1 . [Cl^-]_1 = [Na^+]_2^2 = [Cl^-]_2^2,$$

we obtain

$$(c_1 + x)(x) = (c_2 - x)^2,$$

whence

$$x = \frac{c_2^2}{c_1 + 2c_2}.$$

Dividing through by c_2, we get

$$\frac{x}{c_2} = \frac{c_2}{c_1 + 2c_2},$$

which relation gives us the fraction of NaCl, $\frac{x}{c_2}$, initially present in (2) that has diffused to (1) in terms of the initial concentrations of NaR and NaCl. The following table shows this variation in the distribution of NaCl as a function of the initial concentrations.

TABLE XII

DISTRIBUTION OF NaCl AT EQUILIBRIUM

Initial Concentration of NaR in (1)	Initial Concentration of NaCl in (2)	Initial Ratio of Concentration of NaR to NaCl	Percentage of NaCl Transferred from (2) to (1)	Distribution Ratio of NaCl between (2) and (1)
c_1	c_2	c_1/c_2	$\frac{x}{c_2} \cdot 100$	$\frac{c_2 - x}{x}$
0.01	1	0.01	49.7	1.01
0.1	1	0.1	47.6	1.1
1	1	1	33	2
1	0.1	10	8.3	11
1	0.01	100	1	99

As will be seen from column (4), the amount of NaCl diffusing through the membrane will vary from 50 per cent of the original amount present, when the concentration of NaR is negligible, to only 1 per cent, when the concentration of NaCl is but 1/100 of that of the NaR. The same equilibrium conditions result, of course, regardless of whether we start with NaCl in (2) alone or on both sides of the membrane, or whether we start with both NaR and NaCl on one side of the membrane only. We thus see that the influence of an electrolytically dissociating substance on the permeability of a diffusible substance, despite the non-permeability of the molecule and one ion of the former, is very marked, and may, if present in sufficient quantity, even prevent the normal diffusion of the latter substance.

As Donnan pointed out, this phenomenon must play an important rôle in physiological processes where the presence of the non-dialyzable anions of the salts of the proteins, etc., may modify the diffusibility of ordinary inorganic substances which normally are capable of diffusing through the cell membrane.

Physiological investigations have led to the view that the membranes of many cells show a peculiar elective permeability for ions which is not related to any colloidal character of these ions. Thus Hober[1] concluded that the cells in general showed a variation in permeability towards the anions and cations. The problem of the selective adsorption of drugs by the cells and the influence of electrolytes on this adsorption is but one of the many practical applications of the Donnan Membrane Equilibrium in the medical sciences.

Osmotic Pressure and Membrane Equilibrium: As a result of the unequal distribution of NaCl on the two sides of the membrane considered above, the observed value of the osmotic pressure of NaR is not the true pressure, since the latter is opposed by the pressure exerted by the excess NaCl on the other side of the membrane. Assuming complete dissociation and equal volumes of solution on both sides of the membrane and letting c_1 be the concentration of NaR, P_0, the true osmotic pressure of the NaR, will be given by the equation

$$P_0 = 2c_1RT,$$

since the total concentration of ions from c_1 moles of NaR is $2c_1$, each molecule of NaR dissociating into Na^+ and R^-. If P is the counter pressure due to the unequal distribution of NaCl,

$$P = 2(c_2 - x - x)RT,$$

since the concentration of ions from the NaCl in (2) is $2(c_2 - x)$ and in (1) is $2x$, and hence the excess concentration in (2) is $2(c_2 - x - x)$.

The observed osmotic pressure

$$P_1 = P_0 - P = 2RT[c_1 - (c_2 - 2x)],$$

whence

$$\frac{P_1}{P} = \frac{c_1 - (c_2 - 2x)}{c_1}.$$

But

$$x = \frac{c_2^2}{c_1 + 2c_2},$$

which, when substituted in the above equation, gives

$$\frac{P_1}{P_0} = \frac{c_1 + c_2}{c_1 + 2c_2}.$$

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[1] Höber, Physikalische Chemie der Zelle und Gewebe. Leipzig, 1922.

The numerical relationships between the observed osmotic pressures and those exerted in the absence of an electrolyte, as derived from the last equation, are given below (Table XIII).

TABLE XIII

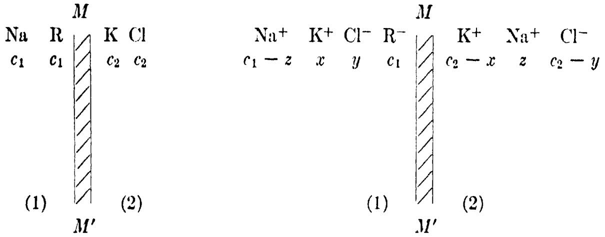
OSMOTIC PRESSURE RATIOS

$\frac{c_1}{c_2}$	$\frac{P_1}{P_0}$	$\frac{c_1}{c_2}$	$\frac{P_1}{P_0}$
0.1	0.92	2	0.60
1	0.67	10	0.52

The observed osmotic pressure of an electrolytically dissociated non-dialyzing substance is thus lowered by the addition of an electrolyte with a common ion, as has been experimentally verified.[1]

Effect of an Electrolyte without Common Ion: The above-described effect in the case of NaCl and NaR is not limited to such cases where we have an ion in common between the electrolyte and non-dialyzing substance, but may be extended by a similar treatment to cases such as NaR and KCl where no such common ion is present.

Beginning with initial concentrations as represented in Fig. 30, the ions of KCl will diffuse from (2) to (1) and the ions of NaCl thus produced in (1) will then diffuse from (1) to (2), to bring about the equilibrium state represented also in Fig. 30. The algebraic subscripts denote ionic concentrations. To satisfy the conditions necessary for electric neutrality, z must be equal to $x - y$, i.e., z, the number of moles of Na^+ transferred from (2) to (1), must equal the algebraic sum of x, the number of moles of K^+ transferred from (2) to (1) minus y, the number of moles of (Cl^-) transferred from (2) to (1).



Initial Condition

Equilibrium Condition

FIG. 30

By a consideration of the work done in small virtual isothermal and reversible changes in the system, we obtain three pairs of variations:

$$1. \quad \begin{cases} \delta n \text{ mol. } Na^+ & (1) \rightarrow (2), \\ \delta n \text{ mol. } K^+ & (2) \rightarrow (1), \end{cases}$$

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[1] Donnan and Harris, *J. Chem. Soc.*, **99**, 1554 (1911). Donnan and Allmand, *ibid.*, **105**, 194 (1914). Donnan and Garner, *ibid.*, **115**, 1313 (1919). Biltz, *Z. physik. Chem.*, **83**, 625 (1913).

in which

$$\delta nRTln\frac{[\mathrm{Na^+}]_1}{[\mathrm{Na^+}]_2} + \delta nRTln\frac{[\mathrm{K^+}]_2}{[\mathrm{K^+}]_1} = 0$$

and

$$\frac{[\mathrm{Na^+}]_1}{[\mathrm{Na^+}]_2} = \frac{[\mathrm{K^+}]_1}{[\mathrm{K^+}]_2}.$$

2. $$\begin{cases} \delta n \text{ mol. Na}^+ & (1) \rightarrow (2), \\ \delta n \text{ mol. Cl}^- & (1) \rightarrow (2), \end{cases}$$

$$\frac{[\mathrm{Na^+}]_1}{[\mathrm{Na^+}]_2} = \frac{[\mathrm{Cl^-}]_2}{[\mathrm{Cl^-}]_1}.$$

3. $$\begin{cases} \delta n \text{ mol. K}^+ & (1) \rightarrow (2), \\ \delta n \text{ mol. Cl}^- & (1) \rightarrow (2), \end{cases}$$

$$\frac{[\mathrm{K^+}]_1}{[\mathrm{K^+}]_2} = \frac{[\mathrm{Cl^-}]_2}{[\mathrm{Cl^-}]_1}.$$

Combining these three results and substituting values of the concentrations, we get

$$\frac{[\mathrm{Na^+}]_1}{[\mathrm{Na^+}]_2} = \frac{[\mathrm{K^+}]_1}{[\mathrm{K^+}]_2} = \frac{[\mathrm{Cl^-}]_2}{[\mathrm{Cl^-}]_1} = \frac{c_1 + c_2}{c_2} = r,$$

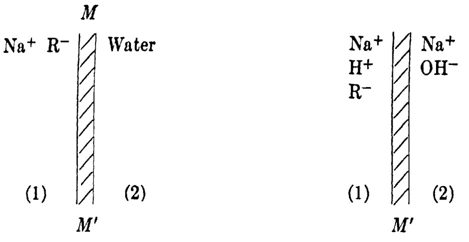
which relation gives us the ratio of the concentrations of any of the dialyzable ions on the two sides of the membrane.

To illustrate this distribution, let us consider the case in which $\frac{c_1}{c_2} = 100$ and therefore $r = 101$. The changes taking place will be:

1. A diffusion of 99 per cent of the K^+ initially present in (2) to (1).
2. A diffusion of only 1 per cent of the Cl^- initially present in (2) to (1).
3. A diffusion of 1 per cent of the Na^+ initially in (1) to (2).

The presence of the NaR has markedly affected the normal distribution of KCl on the two sides of the membrane, having produced a preferential effect whereby practically all the cations of the diffusible electrolyte have been attracted through the membrane and hence show an extraordinary permeability, while the anions on the other hand are expelled.

Hydrolytic Decomposition by Membranes: If we consider the effect of having an aqueous solution of NaR on one side of the membrane and pure water on the other, we find that the NaR will be hydrolyzed. The Na^+ will pass through the membrane since the latter is permeable to it, and in order to maintain electric neutrality, an equivalent amount of (OH^-) from the hydrolytic dissociation of water will diffuse in the same direction, so that the initial and final conditions are represented by Fig. 31. In other words, side (1) will be-



Initial Condition

Equilibrium Condition

Fig. 31

come acid while side (2) will become alkaline, the salt NaR having been hydrolyzed in the process. By following the same considerations as were employed in the development of the previously discussed processes, the extent of this hydrolysis can be expressed by the relation

$$x = \sqrt[3]{K_w c_1},$$

where x is the concentration of the Na^+ that diffuses through the membrane, K_w the ionization constant of water, and c_1 the original concentration of NaR. This equation is derived on the assumption that (1) and (2) occupy equal volumes. If, however, the volume of (2) is v times as great as that of (1), we obtain the corresponding equation

$$x = \sqrt[3]{K_w v^2 c_1}.$$

Despite the small extent of this hydrolysis, it must take place wherever we have a membrane on one side of which is an electrolyte only one of whose dissociation products can diffuse through the membrane into the water on the other side as, e.g., a solution of $K_4Fe(CN)_6$ with a $Cu_2Fe(CN)_6$ membrane. Not only will this hydrolysis affect the observed osmotic pressures of electrolytic colloids but this process also explains the observed removal by dialysis of only one of the ions of an electrolyte adsorbed by a gel. In this case the gel acts as a membrane and if it is permeable to only one of the ions of the electrolyte, this one will pass through and, by continued dialysis, be entirely removed, leaving the other in the form of an acid or base, depending on whether it was the anion or the cation of the electrolyte originally present.

Donnan's theory of membrane equilibrium has also been widely and successfully applied in consideration of the membrane potential difference existing when equilibrium, as brought about by the membrane, has been attained.[1] Inasmuch, however, as this phase of the subject belongs to a consideration of colloids rather than of the laws of dilute solutions, it will not be considered further here.

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[1] See, for example, Loeb, Proteins and the Theory of Colloidal Behaviour, McGraw-Hill Co., 1921.

CHAPTER VIII

HOMOGENEOUS EQUILIBRIA

BY GRAHAM EDGAR, PH.D.,

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Our knowledge of equilibrium and of the "Law of Mass Action" has its beginnings very early in the history of the science, originating in speculations of early investigators as to the cause of chemical action. In the "Tables of Affinity" of Bergmann[1] we find no conception of equilibrium save that of the reversibility of reactions under different physical conditions, as shown by the somewhat different order of the "Affinities" of the elements "in fire" and "in water." Wenzel[2] suggested shortly afterwards that quantity or concentration as well as chemical nature affected the *rate* of chemical action, but this suggestion, which might have had important results, was apparently unnoticed until long afterwards.

The next important step in the development of the subject came in 1799, when Berthollet[3] read certain papers on chemical affinity in which he suggested that large quantity of a material might overcome a weak affinity, and pointed out that the sodium carbonate deposits of Egypt might have been formed from calcium carbonate and salt, the great masses of the latter serving to reverse the usual reaction. This is certainly very nearly a "mass law," but unfortunately Berthollet himself confused the situation by maintaining that mass could affect not only the direction of a reaction but also the ratio in which the substances combine. This brought him into immediate conflict with the law of definite proportions, just then being placed on a firm experimental basis, and in the ensuing controversy Berthollet's conclusions were discredited.

The next advances began to appear, as has been true so frequently in all science, when quantitative experimental investigations began to supplement hypothetical assertions. The investigations of Rose[4] suggested the importance of quantity in affecting chemical action: Wilhelmy[5] made the first quantitative study of the *rate* of a chemical reaction; Malaguti[6] showed that many reactions are reversible, and others added individual facts upon which a theory could be built.

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[1] T. Bergmann, De Attractionibus Electtior's, Upsala (1775).

[2] C. F. Wenzel, Lehre von der Verwandschaft, Dresden, 28 (1777).

[3] C. L. Berthollet, *Memoirs National Institute*, **3** (1799).

[4] *Pogg. Ann.*, **55**, 417 (1842); **82**, 545 (1851); **94**, 481 (1885).

[5] *Pogg. Ann.*, **81**, 413, 499 (1850).

[6] *Ann. Chim. Phys.*, (3) **37**, 198 (1853).

Finally Berthelot and St. Gilles[1] carried out an extensive investigation of the equilibrium between acetic acid, ethyl alcohol, ethyl acetate, and water, and showed that their data could be represented mathematically by the identical expression which the present "Mass law" would give for this reaction.

It remained, however, for Guldberg and Waage[2] to enunciate the generalization which expresses essentially what is commonly called the "law of mass action" of to-day, and to point out clearly the general reversibility of chemical reactions, and the conditions which exist at equilibrium. Guldberg and Waage stated essentially that the rate at which a substance reacts is proportional to its "active mass," and that the rate of a chemical reaction is proportional to the product of the active masses of the substances reacting; thus, if we consider the reaction,

$$A + B = C + D, \tag{1}$$

the rate of the reaction at any given time, from left to right, is given by the expression

$$V_1 = K_1 \times A_A \times A_B, \tag{2}$$

where A_A, etc., represent the active masses of A and B present at that time.

If the reaction is reversible, the rate of the opposing reaction is then

$$V_2 = K_2 \times A_C \times A_D. \tag{3}$$

If both reactions occur simultaneously, a condition will eventually be reached in which $V_1 = V_2$, when, from equations (2) and (3), we have

$$\frac{K_1}{K_2} = K = \frac{A_C \times A_D}{A_A \times A_B}. \tag{4}$$

Equilibrium is thus considered as a dynamic condition, in which two opposing reactions occur at equal rates, and the "equilibrium constant," K, is simply the ratio of the two separate velocity proportionality constants.

Guldberg and Waage recognized the difficulty introduced by the use of the term "active mass," and pointed out that apparently "molecular concentration" could be substituted therefor in the case of dissolved or gaseous substances, and that the active mass of a solid may be considered as constant.

The Condition of Equilibrium in a Chemical Reaction

The Reversibility of Chemical Reactions: Since the time of Guldberg and Waage, numerous experimental investigations have demonstrated the reversibility of particular chemical reactions, and have determined the condition of equilibrium for them under different conditions of temperature and pressure. Furthermore, the application of the principles of thermodynamics to the energy changes accompanying chemical reactions has led to very noteworthy advances in our knowledge of the relations *existing at equilibrium, and many* technical chemical processes of the greatest importance owe their existence to these advances in theory. Nevertheless, there has existed in the literature frequent confusion concerning the fundamental theories underlying the subject. Simplifying assumptions have been made when they could not be expected to be valid; and "laws" containing these assumptions have been widely used, sometimes without apparent realization of the nature of the assumptions involved. The failure of experimental data to conform to these simplified principles has then in many cases led to an unjustified lack of confidence in the fundamental theories involved. Instead, therefore, of considering the subject historically since the time of Guldberg and Waage, it seems preferable to treat in this section the subject of chemical equilibrium from a broad general viewpoint, and to illustrate its actual application to particular cases in a later section. In this treatment we shall speak continually of "reversible" reactions. In the older literature this term is frequently used with reference only to reactions which may have been experimentally carried out in opposite directions. Whereas this use of the term may serve as a convenient method of distinguishing such reactions from those which go to apparent completion in one direction, there is no reason to believe that any reaction is not reversible, at least for the purpose of theoretical considerations. The fact that an equilibrium may lie so far on the side of complete reaction in one direction as to fail of experimental measurement, or the fact that the *rate* of chemical reaction in a given case may be so slow as to prevent the establishment of equilibrium under the conditions investigated, need not prevent us from considering the condition which must prevail at equilibrium in these same reactions. We shall, therefore, consider every reaction as reversible, and as proceeding eventually to a state of equilibrium, which will be determined by the temperature, the pressure (and perhaps other energy factors), and the proportions of the reacting substances.

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[1] *Ann. Chim. Phys.*, (3) **65**, 385 (1862); **66**, 5 (1862); **68**, 225 (1863).

[2] *Forhandlinger i Videnskabs-Selskabet i Christiania*, **35**, 92, 111 (1864). *Etudes sur les affinites chemiques*, Christianja, 1867.

Chemical Equilibrium from the Standpoint of Kinetics: As indicated in the introductory paragraphs, the "Mass law" as derived by Guldberg and Waage was based essentially upon consideration of the kinetics of chemical reactions. It may be noted that for a reaction between dilute gases a statement similar to the equation (4) may be derived from theoretical considerations, based upon the kinetics of moving particles and simple assumptions concerning the relation between the collisions of the reacting species and their combination.

Let us consider the reaction

$$A + B = C + D,$$

where A, B, C, and D are dilute gases. Let us then assume that the number of reactions per unit of time between A and B is proportional to the number of collisions of molecules of A and B in the same time interval. The number of collisions is obviously proportional to the product of the number of molecules of A and the number of molecules of B present in unit volume, or to the product of their partial pressures; thus $N_c = K \times P_A \times P_B$. Since the rate of the reaction between A and B is assumed to be proportional to N_c, we have

$$V_1 = K_1 \times P_A \times P_B,$$

where V_1 is the rate of reaction at a given time, and P_A and P_B the partial pressures of A and B at that time.

Similarly,

$$V_2 = K_2 \times P_C \times P_D.$$

At equilibrium $V_1 = V_2$, hence

$$\frac{K_1}{K_2} = K = \frac{P_C \times P_D}{P_A \times P_B}. \tag{6}$$

If the partial pressures are taken as the "active mass" which is in accordance with the assumptions of Guldberg and Waage, equation (6) is identical with equation (4).

Let us consider the general reaction

$$aA + bB + \cdots = cC + dD \cdots.$$

Since the number of collisions of a molecules of A and b molecules of B per unit of time is given by $N_c = K \times P_A{}^a \times P_B{}^b$, we arrive, by reasoning similar to that just given, at the expression

$$\frac{K_1}{K_2} = K = \frac{P_C{}^c \times P_D{}^d \cdots}{P_A{}^a \times P_B{}^b \cdots}. \tag{7}$$

This equation will be later derived for reactions between dilute gases, from thermodynamic considerations.

The equilibrium constant may thus be regarded, in accordance with the views of Guldberg and Waage, as the ratio between the two velocity constants. Obviously, it should then be calculable from measurements of the two separate reactions. This has, however, seldom been done, as the direct determination of the equilibrium constant is usually more readily accomplished than the measurement of the velocity constants. The relation expressed in equation (7) has been used, however, to determine the *velocity* constant of a reaction from measurement of the equilibrium constant, and the velocity of the reverse reaction.[1]

Since the equilibrium constant is, as shown above, determined by the nature of the reaction as expressed in the equation, while the velocity of the reaction frequently follows a quite obscure course, it seems better on the whole to consider the equilibrium conditions from the thermodynamic view rather than from the kinetic view.

Chemical Equilibrium from the Standpoint of Thermodynamics: The laws of thermodynamics give many relations between the energy changes occurring in "reversible processes" or, in other words, processes conducted in such a way that the system is maintained throughout in a state essentially that of equilibrium; or, in such a way that the direction of the change can be reversed by the expenditure of an infinitesimal quantity of energy. If we grant that chemical reactions are reversible, and that a condition of equilibrium may exist between the reacting constituents, it is clear *that we may apply to such* reactions the laws relating to reversible processes, provided always that we may conceive of a mechanism by which the change can be carried out under proper conditions of equilibrium. Since the energy changes accompanying a reversible process are determined in general by the initial and final states of the system, the deductions of thermodynamics have the advantage that they are independent of the mechanism by which the change is brought about. This, of course, involves the drawback that proof of the mechanism of the change cannot be derived from the final results by thermodynamic reasoning. In applying the principles of thermodynamics to a chemical reaction, therefore, we are concerned with the relations which exist between the proportions of the reacting substances *at the equilibrium condition*, and not with the mechanism by which the condition of equilibrium was attained.

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[1] For an example of this compare Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).

In order to measure the maximum work and the free energy decrease accompanying chemical reactions we shall frequently wish to carry out a process involving the transfer of a gas from one pressure to another, or of a solute from one concentration to another, the process being conducted reversibly throughout.

If we consider a mol. of gas at pressure P_1, the maximum work A which the gas can do in changing to pressure P_2 is given by the equation

$$A = \int_{V_1}^{V_2} PdV. \tag{8}$$

Remembering that

$$\int xdy + \int ydx = xy,$$

we may write equation (8)

$$A = P_2V_2 - P_1V_1 - \int_{P_1}^{P_2} Vdp. \tag{9}$$

Now the free energy increase ΔF accompanying a given change is related to the maximum work by the equation

$$-\Delta F = A - \Sigma P\Delta V, \tag{10}$$

where $\Sigma P\Delta V$ is the net increase in the pressure-volume product which accompanies the change in question.

Combining equations (9) and (10), we obtain

$$\Delta F = \int_{P_1}^{P_2} VdP. \tag{11}$$

If the gas is a perfect gas, we have $PV = RT$, and $P_2V_2 = P_1V_1$, so that

$$A = -\Delta F = RTln\frac{V_2}{V_1} = RTln\frac{P_1}{P_2}. \tag{12}$$

A and $-\Delta F$ are, thus, in this case identical; they are also identical for any change in which the volume is constant; and they are frequently very nearly equal numerically. Nevertheless it is ΔF and not A that is the thermodynamic quantity of greatest importance in considering the condition of equilibrium, for the essential condition of a system in equilibrium is that $\Delta F = 0$ (see Chapter II).

If chemical reaction were in general carried out at constant volume, it would be evidently immaterial whether we calculate A or ΔF, as the two are then equal, but it is nearly always the pressure that is maintained constant and not the volume, so that A and ΔF are apt to differ numerically. We shall, therefore, consider only the free energy increase accompanying given changes in state and not the maximum work.

If we wish to consider the free energy increase accompanying the transfer of a solute from one concentration to another, the calculation may be made as follows: If the solute obeys Henry's law, that is, if its partial pressure above the liquid is proportional to its mol. fraction, we may transfer it from one concentration to another by a three step process.

1. The first step will be to vaporize one mol. of it from a very large quantity of the solution of mol. fraction X_1 at its partial pressure P_1 $(= KX_1)$. Since the system is in equilibrium during this process, $\Delta F_1 = 0$.

2. We may then change the pressure reversibly from P_1 to P_2 $(= KX_2)$. The free energy increase for this step is (equation 11)

$$\Delta F_2 = \int_{P_1}^{P_2} VdP. \tag{13}$$

3. We may then introduce the vapor into a large quantity of the solution whose mol. fraction is X_2, and since this also involves a system in equilibrium, $\Delta F_3 = 0$.

The entire free energy increase is then given by ΔF_2, and if the vapor obeys the gas laws, we have

$$\Delta F = RT\,ln\frac{P_2}{P_1} = RT\,ln\frac{X_2}{X_1}\cdot \tag{14}$$

Similarly, if the solution obeys Henry's law, and is also so dilute that the mol. fraction is proportional to its molecular concentration, or to its molality (concentration in mols. per 1000 grams of solvent), we may write, for a change from C_1 to C_2 or from M_1 to M_2,

$$\Delta F = RT\,ln\frac{C_2}{C_1}; \qquad \Delta F = RT\,ln\frac{M_2}{M_1}\cdot \tag{15}$$

The relations which must exist at equilibrium in a chemical reaction may now be simply derived for cases in which the laws of perfect gases or of perfect solutions are valid.

Derivation of the Mass Law for a Gaseous System: Let us consider the following reaction between the substances A, B, C, and D, etc., according to the equation

$$aA + bB\cdots = cC + dD\cdots.$$

Let us take two different equilibrium systems I and II, at the same temperature, produced by allowing two different mixtures of the reacting substances to come to equilibrium, and let these two systems be so large that removal of small quantities of the reacting species does not alter their composition appreciably. Furthermore, let us suppose the two systems to be contained in vessels provided with membranes permeable only to A, B, C, and D, respectively, leading to cylinders provided with pistons, by means of which any given component of the mixture may be withdrawn or added to either system.

Step (1). Let us withdraw from reservoir (I) a mols. of A and b mols. of B at the partial pressures P_{1_A} and P_{1_B}, at which they are present in the equilibrium system (I). The free energy increase for this step is evidently zero, since the condition of equilibrium is not measurably disturbed.

Step (2). Let us change, reversibly, the pressures of the two gases to P_{2_A} and P_{2_B}, at which they exist in the second equilibrium system. The free energy increase for this step is evidently, since the gas laws are obeyed,

$$\Delta F_1 = aRTln\frac{P_{2_A}}{P_{1_A}} + bRTln\frac{P_{2_B}}{P_{1_B}}\,. \tag{16}$$

Step (3). We may now introduce the gases into the equilibrium system II, and since this does not measurably disturb the equilibrium, we have again zero free energy increase.

Steps (4), (5), and (6). Let us carry out a similar series of steps by which we remove c mols. of C and d mols. of D from system II, change their partial pressures from P_{2_C} and P_{2_D} to P_{1_C} and P_{1_D}, and introduce them into system I. The total free energy increase is then, as above,

$$\Delta F_2 = cRTln\frac{P_{1_C}}{P_{2_C}} + dRTln\frac{P_{1_D}}{P_{2_D}}\,. \tag{17}$$

Steps 1, 2 and 3, and 4, 5, and 6 are supposed to be carried out at corresponding times, and so slowly that the A and B removed from system I react in system II to replace the C and D which have been removed therefrom, which in turn react in system I to form A and B. If this has been the case, the entire composition of each system is just what it was at the beginning of the process, and as each step has been carried out isothermally and reversibly, the total free energy increase must be zero (Chapter II).

Therefore,

$$\Delta F_1 + \Delta F_2 = 0,$$

and, from equations (16) and (17),

$$aRTln\frac{P_{2_A}}{P_{1_A}} + bRTln\frac{P_{2_B}}{P_{1_B}} + cRTln\frac{P_{1_C}}{P_{2_C}} + dRTln\frac{P_{1_D}}{P_{2_D}} = 0. \tag{18}$$

Or, rearranging,

$$RTln\frac{P^c_{2_C} \times P^d_{2_D}\cdots}{P^a_{2_A} \times P^b_{2_B}\cdots} = RTln\frac{P^c_{1_C} \times P^d_{1_D}\cdots}{P^a_{1_A} \times P^b_{1_B}\cdots}, \tag{19}$$

whence

$$\frac{P^c_{2_C} \times P^d_{2_D}\cdots}{P^a_{2_A} \times P^b_{2_B}\cdots} = \frac{P^c_{1_C} \times P^d_{1_D}\cdots}{P^a_{1_A} \times P^b_{1_B}\cdots} \tag{20}$$

or

$$\frac{P_C{}^c \times P_D{}^d\cdots}{P_A{}^a \times P_B{}^b\cdots} = K. \tag{21}$$

Equation (21) is identical, for a dilute gaseous system, with the mass law of Guldberg and Waage, and with that obtained previously (equation 7) from kinetic considerations.[1]

Equation (21) was derived for a dilute gaseous system. If, however, we consider the reaction as occurring between substances in solution, we may readily derive a similar equation for any substance in solution whose vapor obeys Henry's law and the simple gas law. The procedure is identical with that employed in deriving equation (21) except that the two equilibrium systems are liquid, and the transfer of each solute from one concentration to the other is done by first vaporizing it from the solution. The free energy change for each mol. transferred is given by equation (14), and the final result is that

$$K = \frac{X_C{}^c \times X_D{}^d\cdots}{X_A{}^a \times X_B{}^b\cdots}. \tag{22}$$

Similarly, if the solution is quite dilute, we may write (compare equation 15)

$$K = \frac{C_C{}^c \times C_D{}^d\cdots}{C_A{}^a \times C_B{}^b\cdots}. \tag{23}$$

Equations (22) and (23) may also be derived by consideration of the osmotic work involved in the transfer of material from one concentration to another, making use of the relation that $P_0 = CRT$, where C is the molecular concentration.

Equations (21), (22) and (23) constitute the mass laws ordinarily employed. They express the relations which may be expected to exist at equilibrium at any given temperature, provided the reacting substances are gases sufficiently dilute to obey the gas laws, or ideal or sufficiently dilute solutions. Now the gas laws are actually approximately valid for a large number of gases under conditions in which they are apt to occur in chemical reactions, but the ideal solution laws are valid for only a very small fraction of the solutions which are apt to be employed. If the simple laws are not assumed, it would be necessary to know the "equation of state" of each reacting substance in order to derive a statement of the concentrations which might be expected to prevail under different conditions of equilibrium. The derivation of a simple mass law in terms of partial pressures, concentrations, etc., in the case of a general reaction between gases, liquids and solids, and assuming no equations of state, cannot be accomplished. For many purposes it is convenient to consider the question of equilibrium in chemical reactions from the standpoint of the *activities*[1] of the reacting species.

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[1] *Note:* In writing mass law expressions, it has become an established convention to write in the *numerator* the partial pressures, concentrations, etc., of the substances appearing on the right hand side of the chemical equation. In order to avoid confusion, this procedure should be rigidly followed.

The activity is defined essentially by the equation

$$F_A = RT ln a_A + C_A, \tag{24}$$

where F_A is the molal free energy of the substance A under given conditions, a_A is its activity, and C_A is a constant which may be arbitrarily defined. (In *Lewis and Randall*, C_A is called F_0, "the molal free energy in the standard state," the "standard state" of a substance being selected arbitrarily for different types of reaction.) A full discussion of this useful function will not be given here, but it may be pointed out, in order to illustrate the general nature of the "activity," that the activity of a perfect gas is equal to its pressure, and for any actual gas the activity approaches the pressure as the gas becomes dilute; the activity of a solute is equal to its mol. fraction when the solution is sufficiently dilute. In the case of aqueous solutions the activity is frequently defined to approach the molality instead of the mol. fraction when the solution becomes dilute. If it is desired to visualize the term, it may perhaps be thought of as the "apparent concentration" or "effective concentration" which may not be identical with the actual concentration.

The increase in free energy when a substance changes from one set of conditions to another is given from equation (24) by the equation

$$\Delta F_A = RT ln \frac{a_A'}{a_A}, \tag{25}$$

where a_A and a_A' represent the activities in the initial and final states respectively, and ΔF_A represents the increase in free energy accompanying the change.

Derivation of the Mass Law in Terms of Activities: Let us consider again the general reaction

$$aA + bB \cdots = cC + dD \cdots, \tag{26}$$

where A, B, C, and D may be either gases, dissolved substances, liquids or solids. The essential criterion that a condition of equilibrium exists in any process at constant temperature is that the free energy increase for the process shall be zero. For the reaction (26), at the condition of equilibrium, the sum of the molal free energies of A and B must be equal to the sum of the molal free energies of C and D; that is,

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[1] See Chapter XII, and Lewis and Randall, Thermodynamics and Chemistry (McGraw-Hill Co., 1923).

$$aF_A + bF_B \cdots = cF_C + dF_D \cdots. \tag{27}$$

Combining equations (24) and (27), we have, if we consider the activities of the reacting substances in the equilibrium mixture,

$$\begin{aligned} aRTlna_A + aC_A + bRTlna_B + bC_B \cdots \\ = cRTlna_C + cC_C + dRTlna_D + dC_D \cdots \end{aligned} \tag{28}$$

or

$$aC_A + bC_B - cC_C - dC_D \cdots = RTln\frac{a_C{}^c \times a_D{}^d \cdots}{a_A{}^a \times a_B{}^b \cdots}. \tag{29}$$

Since the quantities on the left hand side of the equation are constants, fixed by the definition of the standard state, we may for any given temperature write equation (29)

$$K_a = \frac{a_C{}^c \times a_D{}^d \cdots}{a_A{}^a \times a_B{}^b \cdots}, \tag{30}$$

where K_a may be called the equilibrium constant in terms of the activities of the reacting constituents. This equation has been derived without any simplifying assumptions and may be regarded as perfectly general for any chemical reaction whatever.

It will be noted that equation (30) is quite similar to that originally proposed by Guldberg and Waage (4) except that the quite indefinite term "active mass" is replaced by the thermodynamically defined term "activity." In order to express equation (30) in terms of some experimentally measurable composition term, we must find a relation between the activity of each constituent and its partial pressure, mol. fraction, concentration, etc.

Fortunately, in many cases, relationships exist which enable us to derive approximate "mass laws" for practical application. Thus, for dilute gaseous systems, we have the activity approximately equal to the pressure, and by substituting in equation (30) $P = a$, we obtain

$$K_p = \frac{P_C{}^c \times P_D{}^d \cdots}{P_A{}^a \times P_B{}^b \cdots}, \tag{31}$$

which is evidently identical with equation (21) previously derived for gaseous systems. Since partial pressure (partial pressures should always be expressed in atmospheres), is defined by the relation $P_A = X_AP$, where X represents mol. fraction and P total pressure, we may also write

$$K_p = \frac{X_C{}^c \times X_D{}^d}{X_A{}^a \times X_B{}^b} \times P^{(c+d-a-b)\cdots}, \tag{32}$$

or, at any given pressure,

$$K_x = \frac{X_C{}^c \times X_D{}^d}{X_A{}^a \times X_B{}^b}, \tag{33}$$

where

$$K_x = K_p \times P^{(a+b-c-d)}. \tag{34}$$

Since for dilute gases we also have the relationship $PV = NRT$, and $\frac{N}{V} = C$, the concentration in mols. per liter, equation (30) may be written

$$K_p = \frac{C_C{}^c \times C_D{}^d \cdots}{C_A{}^a \times C_B{}^b \cdots} \times (RT)^{(c+d-a-b)},$$

whence

$$K_c = \frac{C_C{}^c \times C_D{}^d \cdots}{C_A{}^a \times C_B{}^b \cdots}, \tag{35}$$

where

$$K_c = K_p \times (RT)^{(a+b-c-d)}. \tag{36}$$

Combining equations (34) and (36), we obtain

$$K_c = K_x \cdot \left(\frac{RT}{P}\right)^{(a+b-c-d)} = K_x \cdot \left(\frac{V}{N}\right)^{(a+b-c-d)}. \tag{37}$$

The numerical relationships between the three constants are given by equations (34), (36) and (37), from which it is clear that when $a + b = c + d$ the three constants are numerically equal. The selection of a particular equation in any given case depends frequently upon convenience in considering the data in question.

It should be noted that K_p and K_c are independent of the pressure, within the limits in which the gas laws are obeyed. At high pressures none of the equations may be expected to be exactly valid

In applying equation (30) to equilibrium in homogeneous liquid systems, we find in general much greater difficulty in relating the activity of the constituents of an equilibrium mixture to their concentration than is true in the case of gases.

In the case of a "perfect solution," we may equate the activity at atmospheric pressure to the mol. fraction, and obtain an equation identical with equation (32), or

$$K_x = \frac{X_C{}^c \times X_D{}^d \cdots}{X_A{}^a \times X_B{}^b \cdots}. \tag{38}$$

Remembering that the concentration in mols. per liter is related to the mol. fraction by the equation

$$C = X \times \frac{V}{N}, \tag{39}$$

where V is the total volume and N the total number of mols. (including indifferent, or solvent, mols.) contained therein, we may write equation (38) as

$$K_x = \frac{C_C{}^c \times C_D{}^d \cdots}{C_A{}^a \times C_B{}^b \cdots} \times \left(\frac{N}{V}\right)^{(c+d-a-b)}. \tag{40}$$

If the number of indifferent mols., say of solvent, becomes quite large in comparison with the number of mols. of reacting constituents, neither V nor N will change greatly with changes in the concentrations of the reacting species and we may write, for a dilute solution,

$$K_c = \frac{C_C{}^c \times C_D{}^d \cdots}{C_A{}^a \times C_B{}^b \cdots}. \tag{41}$$

In aqueous solution, many data are at present available in the form of molalities, or mols. per 1000 grams of water. The molality is related to the concentration by the equation

$$M = C \cdot \frac{V}{k}, \tag{42}$$

where k is the number of kilograms of water contained in V liters of solution. Obviously, in dilute solutions, V/k approaches unity.

If we substitute molalities for concentrations in equation (41), we obtain

$$K_c = \frac{M_C{}^c \times M_D{}^d \cdots}{M_A{}^a \times M_B{}^b \cdots} \times \left(\frac{V}{k}\right)^{(c+d-a-b)} \tag{43}$$

or

$$K_m = \frac{M_C{}^c \times M_D{}^d \cdots}{M_A{}^a \times M_B{}^b \cdots}. \tag{44}$$

Equations (38), (41) and (44) are most frequently employed in the treatment of equilibrium in homogeneous liquid media.

The numerical relations existing between the constants K_x, K_c, and K_m, for equilibria in liquid media, are evidently

$$K_x = K_c \cdot \left(\frac{N}{V}\right)^{(c+d-a-b)}, \tag{45}$$

$$K_c = K_m \cdot \left(\frac{V}{k}\right)^{(c+d-a-b)}. \tag{46}$$

When $a + b = c + d$, the three constants are numerically identical, while K_c and K_m are very nearly identical for any dilute solution.

It is difficult to predict the extent to which equations (38), (41) and (44) may be expected to be valid in any given case. Many organic substances, particularly those similar in chemical constitution, generally approximate to the behavior of "perfect solutions" over a wide range of concentrations. On the other hand, solutions of highly ionized substances are so far from "perfect" that their behavior deserves special treatment (Chapters XI and XII). In general, the more nearly alike in composition substances entering into reaction may be, and the more dilute the solution in which they react, the more nearly the mol. fraction or molality is apt to measure the activity, and the more nearly the equilibrium laws of solutions are apt to be valid. The subject will be treated further in a later section.

We have gone into the various equilibrium constants in considerable detail, because considerable confusion sometimes results from the use of different "mass laws" without an understanding of the assumptions underlying their derivation, and of their relations to each other. All of the equations evidently express relations which represent a limiting condition which may be approximated under actual conditions.

In pages 296 to 302 we have derived a series of mass laws identical with those derived directly in pages 292 to 294, and actually involving identical assumptions concerning the behavior of the reacting constituents. The difference has been only one of method. Equations (33), (35), (37), (38), (41) and (44) were derived from the "universally valid" equation (30) by means of essentially the same simplifying assumptions that were employed in the preceding section.

It may be objected that when we speak of equation (30) as "universally valid" we are reasoning in a circle, as it is valid only because of the definition of the term "activity," and that since no simple general relation exists between the activity of a substance and its pressure or concentration, the equation has no real significance. In a sense this is certainly correct; nevertheless, there are important advantages in the use of the "activity" in the treatment of equilibrium.

If we do not utilize some such function, we can only derive various "mass laws" valid for limiting conditions, and in any actual case outside of these conditions we can only say that "the mass law does not hold." The use of an equation which is universally valid accomplishes several purposes. In the first place it emphasizes the limitations that are actually involved in all of the simpler mass laws, and these limitations are frequently overlooked; it furnishes a convenient basis for the investigation of equilibrium in cases in which the simple mass laws do not apply (particularly in such cases as involve highly ionized substances); and, in mathematical treatment involving the combination of different reactions, it furnishes an expression which may be combined with other similar expressions without involving assumptions which might be easily overlooked and which might complicate the mathematical treatment. Furthermore, the use of equation (30) emphasized the thermodynamic view that the condition of equilibrium is defined by the statement that the free energy increase at equilibrium must be equal to zero, and that any mass law is directly or indirectly an expression of this fact.

We shall therefore regard equation (30) as "the mass law," although we actually employ in most cases the simple equations derived therefrom.

THE INCREASE IN FREE ENERGY ACCOMPANYING A CHEMICAL REACTION

The increase in free energy accompanying a chemical reaction is an important thermodynamic function, which will be employed in later sections of this chapter in the derivations of relations expressing the variation of the equilibrium constant with the temperature and pressure. In order to calculate the increase in free energy for any given chemical reaction, we must devise a mechanism by which, theoretically at least, the reaction can be caused to occur isothermally and reversibly.

The Free Energy Increase in a Reaction between Dilute Gases: Let us consider the reaction

$$aA + bB \cdots = cC + dD \cdots,$$

in which the reacting substances are dilute gases. Let the initial partial pressures of A and B be represented by P_A and P_B, and the final partial pressures of C and D by P_C and P_D.

We wish to carry out the reaction in a series of isothermal reversible steps. Let us imagine that a mols. of the substance A and b mols. of B, at partial pressures P_A and P_B, respectively, are contained in separate cylinders fitted with frictionless pistons, and provided with membranes, which can be opened when desired, permeable only to A and B, respectively.

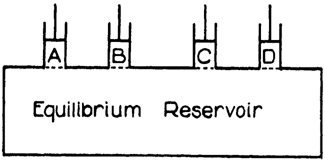

Fig. 1

Let us also imagine an indefinitely large reservoir containing A, B, C, and D in the proportions in which they exist in chemical equilibrium, their partial pressures being P_A', P_B', P_C', and P_D', respectively. The semi-permeable membranes of the cylinders of A and B open when desired into this reservoir. Similar membranes permeable only to C and D are open to cylinders which are to contain these substances. A diagram of the arrangement is given in Fig. 1.

Step 1.—Change the pressure of A, in the cylinder containing it, isothermally and reversibly from P_A to P_A', involving the increase in free energy, $a \int_{P_A}^{P_A'} VdP$. Change similarly the partial pressure of B from P_B to P_B', with the free energy increase, $b \int_{P_B}^{P_B'} VdP$.

Step 2.—Open the connections of the cylinders of A and B into the equilibrium reservoir, and introduce through the semi-permeable membranes a mols. of A and b mols. of B, at their partial pressures P_A' and P_B'.

Simultaneously withdraw from the reservoir c mols. of C and d mols. of D, at the partial pressures P_C' and P_D'. During this process the A and B introduced into the reservoir react to form C and D, thus keeping the composition of the reservoir only infinitesimally different from the equilibrium condition.

Since the partial pressures of A, B, C, and D in the cylinders were equal to the corresponding pressures in the reservoir, none of the processes occurring in Step 2 have involved any change in free energy.

Step 3.—Change, isothermally and reversibly, the partial pressures of C and D in the cylinders containing them, from P_C' to P_C and from P_D' to P_D, respectively. This involves the free energy increases $c\int_{P_C'}^{P_C} VdP$ and $d\int_{P_D'}^{P_D} VdP$.

The net result of steps (1), (2), and (3) is the occurrence of the chemical reaction as required by the reaction equation and each step has been carried out isothermally and reversibly. The sum of the various free energy increases must be, therefore, the total free energy increase of the reaction, which is the quantity which we desired to derive. We may then write

$$\Delta F = a\int_{P_A}^{P_A'} VdP + b\int_{P_B}^{P_B'} VdP + c\int_{P_C'}^{P_C} VdP + d\int_{P_D'}^{P_D} VdP.$$

Now, if the gases are sufficiently dilute for the gas laws to be valid, we may write

$$\Delta F = aRTln\frac{P_A'}{P_A} + bRTln\frac{P_B'}{P_B} + cRTln\frac{P_C}{P_C'} + dRTln\frac{P_D}{P_D'} \qquad (47)$$

or, rearranging,

$$\Delta F = RTln\frac{P_C{}^c \times P_D{}^d \cdots}{P_A{}^a \times P_B{}^b \cdots} - RTln\frac{P_C'{}^c \times P_D'{}^d \cdots}{P_A'{}^a \times P_B'{}^b \cdots}. \qquad (48)$$

Recalling equation (31), equation (48) becomes

$$\Delta F = RTln\frac{P_C{}^c \times P_D{}^d}{P_A{}^a \times P_B{}^b} - RTlnK_p. \qquad (49)$$

The free energy increase for a dilute gaseous reaction is evidently determined at constant temperature by the equilibrium constant, and by the initial and final partial pressures of the reacting species. If the latter should be each equal to unity, we have

$$\Delta F = -RTlnK_p. \qquad (50)$$

The free energy increase for a reaction between perfect solutes in solution may be derived in an exactly similar way. However, it is preferable to consider the most general case, involving the activities of the reacting species.

Let us consider again the general reaction

$$aA + bB \cdots = cC + dD \cdots, \qquad (51)$$

in which A, B, C, and D may be substances in any state whatever. Let a_A, a_B, etc., represent the activities of the reactants in the specified initial states, and a_C, a_D, etc., the activities of the resultants in the specified final states. The corresponding activities at the equilibrium state are a_A', a_B', a_C', and a_D'. We may imagine the reaction as being brought about by a mechanism similar to that outlined above for a gaseous system. Remembering that the free energy increase in changing a mol. of substance from activity a to activity a' is equal to $RTln(a'/a)$, and that the free energy increase at the condition of equilibrium is equal to zero, we may write for the free energy increase accompanying reaction (51)

$$\Delta F = RTln\frac{a_C{}^c \times a_D{}^d \cdots}{a_A{}^a \times a_B{}^b \cdots} - RTln\frac{a_C{}'^c \times a_D{}'^d \cdots}{a_A{}'^a \times a_B{}'^b \cdots} \cdot \qquad (52)$$

This may be written, remembering equation (30),

$$\Delta F = RTln\frac{a_C{}^c \times a_D{}^d}{a_A{}^a \times a_B{}^b} - RTlnK_a \qquad (53)$$

or, for the reactions in which the initial activities of the reactants and the final activities of the resultants are each equal to unity, we have

$$\Delta F = -RTlnK_a. \qquad (54)$$

The free energy increase represents an extremely useful function in considering the thermodynamics of chemical reactions. If we can determine the value of ΔF for a given reaction under given conditions, we can predict whether or not the reaction may occur spontaneously, since spontaneous change can occur only in the direction of a decrease in free energy. A negative value of ΔF, therefore, for a chemical reaction written in a given sense indicates that spontaneous reaction is possible in that sense; a positive value indicates that the reaction can occur only in the opposite sense. Furthermore we may employ equations (53) and (54) either to calculate ΔF when the equilibrium constant is known, or to calculate the equilibrium constant when ΔF is known. In addition to the relations expressed in equations (53) and (54), the free energy increase for a chemical reaction may be determined from the electromotive force of reversible cells (see Chapter XII), and through the third law of thermodynamics, from the entropies of the reacting substances (Chapter XVII). The calculation of free energy data by these different methods, and the combination of the data from all sources, has yielded so much valuable information that it is highly desirable that systematic determinations of the free energy changes of chemical reactions should be made, and the data expressed in unified form. In order to avoid confusion, it is necessary that unity of procedure should be followed in making the fundamental definitions of the quantities involved in the calculations. The most complete systematic calculations of free energy appear in the recent work by Lewis and Randall to which reference has already been made, and it seems advisable to adopt essentially their usage. They define the activity of a substance in such a way that for a pure chemical substance the activity is unity at atmospheric pressure, for that form of the substance stable under the prevailing conditions. For a solute, the activity is defined, for non-electrolytes, by the relation $a/x = 1$ when x becomes equal to zero or as the solution approaches infinite dilution.

For solutions of electrolytes a special definition of activity is employed which is discussed in Chapter XII. The free energy increase of a chemical reaction, as calculated from the equilibrium constant by equation (54), refers to a change of state in which either pure solids, liquids and gases occur in the equation, at atmospheric pressure, or in which dissolved substances are present in such concentration that their activity is equal to unity.

It should be emphasized that it is K_a which measures the free energy change, and not K_p, K_x or K_c unless the conditions are such that these equilibrium constants are equal to K_a. Thus, in order to calculate free energy change from equilibrium data, we must either make the measurements in solutions so dilute, or at gas pressures so low, that the activities of the reacting species are approximately given by their mol. fraction, partial pressures, etc.; or we must make measurements over a sufficient range of concentrations to permit extrapolation with reasonable certainty into the desired range of conditions. The calculation of free energy data and of equlibrium constants from free energy data will be treated briefly in a later section; for a complete discussion reference should be made to Lewis and Randall's Thermodynamics and Chemistry.

THE VARIATION OF EQUILIBRIUM CONDITIONS WITH TEMPERATURE, PRESSURE, AND CONCENTRATION

The Le Chatelier-Braun Principle: A state of equilibrium in a chemical reaction is determined by the temperature, the pressure, and the proportions of the substances present. We wish frequently to know, both qualitatively and quantitatively, the change in the condition of equilibrium which will be brought about by a change in one or more of the variable factors involved.

Qualitatively, these changes may be predicted by the use of the theorem of Le Chatelier-Braun, which may be stated as follows: If a change occurs in one of the factors determining a condition of equilibrium, the equilibrium shifts in such a way as to tend to annul the effect of the change. From this statement it follows that the effect of an increase in temperature, all other factors remaining constant, is to shift an equilibrium in the direction in which *absorption of heat* occurs, as this change would tend to annul the effect of the heat added in changing the temperature; the effect of an increase in pressure will be to shift the equilibrium in the direction in which a *decrease in volume* occurs, as this change would tend to annul the effect of the increased pressure; an increase in the concentration of one of the substances present at equilibrium will shift the equilibrium in such a way as to tend to decrease the concentration of that substance. This principle is an extremely useful one, and serves not only for purely qualitative predictions, but also as a check upon the quantitative results in which errors of calculation may appear.

The quantitative information is, of course, usually more important and will be treated at length below, but it is instructive to consider the results of every quantitative calculation in the light of the Le Chatelier-Braun principle.

The Effect of Temperature upon Chemical Equilibrium: The combination of the first and second laws of thermodynamics gives us for a reversible change the Gibbs-Helmholz equation (Chap. II)

$$\Delta A - \Delta U = T\left(\frac{d(\Delta A)}{dT}\right)_v. \qquad (55)$$

In this equation it is assumed that the initial and final volumes are not functions of the temperature. Since in most chemical reactions pressure rather than volume is fixed by the conditions assumed for the reaction, it is preferable to write equation (55) in terms of the free energy increase and the increase in heat content, so that it becomes

$$\Delta F - \Delta H = T\left(\frac{d(\Delta F)}{dT}\right)_p. \tag{56}$$

Equation (53) gives us, for any reaction at constant temperature,

$$\Delta F = RTln\frac{a_C^c \times a_D^d \cdots}{a_A^a \times a_B^b \cdots} - RTlnK_a, \tag{57}$$

where K_a is the equilibrium constant and a_A, etc., represent the activities of the reacting constituents in the specified initial and final states.

Combining (56) and (57), and rearranging, we obtain

$$\frac{d(\Delta F)}{dT} = -\frac{\Delta H}{T} - RlnK_a + Rln\frac{a_C^c \times a_D^d \cdots}{a_A^a \times a_B^b \cdots}. \tag{58}$$

Differentiating (57) with respect to T and remembering that since the values of a are arbitrarily chosen and not determined by temperatures, the expression

$$RTdln\left(\frac{a_C^c \times a_D^d \cdots}{a_A^a \times a_B^b \cdots}\right)\bigg/ dT$$

is equal to zero, we have

$$\frac{d(\Delta F)}{dT} = -RlnK_a - RT\frac{dlnK_a}{dT} + Rln\frac{a_C^c \times a_D^d \cdots}{a_A^a \times a_B^b \cdots}. \tag{59}$$

Equating the right hand members of (58) and (59) and simplifying, we have

$$\frac{dlnK_a}{dT} = \frac{\Delta H}{RT^2}. \tag{60}$$

This important equation, usually called the equation of van't Hoff, expresses quantitatively the change of the general "mass law" equilibrium constant with the temperature, as a function of ΔH, which is equal to $-Q_p$, where Q_p is the heat evolved by the reaction at constant pressure. Under conditions in which the special mass laws (equations (31), (33) and (38), (41), (44)) may be expected to be valid, equation (60) may be modified by combining it with the relation between K_a and the equilibrium constant in question.

Thus, under conditions in which $P = a$, we have

$$\frac{dlnK_p}{dT} = -\frac{Q_p}{RT^2}. \tag{61}$$

Since $K_p = K_c(RT)^{-n}$, where $n = a + b - c - d$ (equation (36)), we may write

$$ln K_p = ln K_c - n ln RT \tag{62}$$

and, combining with (61),

$$\frac{d ln K_c}{dT} - \frac{n d ln RT}{dT} = -\frac{Q_p}{RT^2} \tag{63}$$

or

$$\frac{d ln K_c}{dT} = -\frac{Q_p}{RT^2} + \frac{n}{T} = -\frac{Q_p - nRT}{RT^2} = -\frac{Q_v}{RT^2}. \tag{64}$$

Similarly, making use of equation (34),

$$K_p = K_x \cdot P^n \tag{65}$$

and

$$\frac{d ln K_x}{dT} + \frac{d ln P^n}{dT} = -\frac{Q_p}{RT^2}. \tag{66}$$

For reactions at constant pressure, P, therefore, equation (66) becomes

$$\frac{d ln K_x}{dT} = -\frac{Q_p}{RT^2}. \tag{67}$$

Equation (60) may be integrated if ΔH is independent of temperature or may be represented as a function of temperature. In the first case we obtain

$$ln K_a = -\frac{\Delta H}{RT} + C, \tag{68}$$

or, between T_1 and T_2,

$$ln K_{1_a} - ln K_{2_a} = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{69}$$

Changing to ordinary logarithms and inserting the numerical value of R, equation (69) becomes

$$log\, K_1 - log\, K_2 = -\frac{\Delta H}{4.5787}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{70}$$

This equation is widely used for the calculation of the effect of temperature upon equilibrium in cases where the heat of reaction is known, and for the calculation of the heat of reaction where the equilibrium constant is known at more than one temperature. Even if ΔH is really dependent upon temperature, equation (70) usually gives approximately correct results if the interval between T_1 and T_2 is not too great.

In general, the variation of ΔH with T is given by the Kirchoff formula (Chap. II),

$$\frac{d(\Delta H)}{dT} = \Delta C_p, \tag{71}$$

where ΔC_p represents the difference between the heat capacities of the substances on the right hand side of the equation for the chemical reaction and those of the left. It is frequently possible to express the heat capacities of each substance as a series function of temperature, of the form

$$C_p = m + nT + oT^2 \cdots. \qquad (72)$$

In this case, considering again the reaction

$$aA + bB \cdots = cC + dD \cdots, \qquad (73)$$

we have

$$\Delta C_p = (cm_C + dm_D - am_A - bm_B) + (cn_C + dn_D - an_A - bn_B)T + (co_C + do_D - ao_A - bo_B)T^2 \cdots \qquad (74)$$

or,

$$\Delta C_p = q + rT + sT^2 \cdots, \qquad (75)$$

where q, r and s represent the terms in the parentheses, and are numerical constants for any given reaction.

Combining (71) and (75), we obtain

$$\frac{d(\Delta H)}{dT} = (q + rT + sT^2 \cdots) \qquad (76)$$

and, integrating,

$$\Delta H = \Delta H_0 + qT + \tfrac{1}{2}rT^2 + \tfrac{1}{3}sT^3 \cdots. \qquad (77)$$

The integration constant is called ΔH_0, since it is the value which ΔH reaches in equation (77) if T is made equal to zero.

If we combine equations (77) and (60), we obtain

$$\frac{dlnK_a}{dT} = \frac{\Delta H_0}{RT^2} + \frac{q}{RT} + \frac{1}{2}\frac{r}{R} + \frac{1}{3}\frac{s}{R}T \cdots \qquad (78)$$

or

$$lnK_a = -\frac{\Delta H_0}{RT} + \frac{q}{R}lnT + \frac{1}{2}\frac{r}{R}T + \frac{1}{6}\frac{s}{R}T^2 \cdots + C. \qquad (79)$$

Equation (79) expresses accurately the effect of temperature upon chemical equilibrium, and should always be employed in making calculations over a wide temperature interval, provided the necessary data concerning the heat capacities of the reacting substances are available.

If we combine equation (79) with equation (54), we obtain

$$\Delta F = \Delta H_0 - qTlnT - \tfrac{1}{2}rT^2 - \tfrac{1}{6}sT^3 \cdots - C'T, \qquad (80)$$

which expresses the change of the "standard" free energy increase of a reaction with change in temperature. This equation is an extremely important one in the systematic calculation of free energy data.

Very frequently accurate data concerning the heat capacities of the reacting substances over a wide range of temperature are not available, but values of the equilibrium constant at a number of temperatures are available. In this case it is often possible to express the variation of the equilibrium constant with the temperature by means of empirical formulæ, usually corresponding in type to equation (79), and differing only in the numerical values of the constants. Several different equations may express given numerical data over certain temperature ranges almost equally well, and may serve for the practical calculation of the equilibrium constant at temperatures differing from those measured. It is desirable, however, to utilize in all calculations equation (79), containing actual specific heat data, wherever these are available. Specific examples of these formulæ, both of the empirical type and those employing exact specific heat data, will be given in a later section.

The Effect of Pressure upon Chemical Equilibrium: Quantitatively the effect of pressure change upon chemical equilibrium may be followed by considering the various equilibrium constants. The activity constant, K_a, is necessarily independent of the pressure, as may be seen from its relation to the free energy change in the reaction, occurring between certain defined initial and final states. Since these initial and final states are arbitrarily defined and independent of the pressure, the free energy increase and K_a must be independent of the pressure. For a reaction between dilute gases, $K_a = K_p$, which is also independent of pressure, as is K_c, which is related to K_p by a factor not dependent upon pressure. The equilibrium constant, K_x, however, varies with the pressure. Writing from equation (34)

$$K_x = K_p \times P^{(a+b-c-d)} \tag{81}$$

and taking logarithms, we have

$$ln\ K_x = ln\ K_p + (a + b - c - d)\ ln\ P. \tag{82}$$

Differentiating with respect to P, we obtain

$$\frac{dlnK_x}{dP} = \frac{(a + b - c - d)}{P}. \tag{83}$$

When $PV = RT$, this expression becomes

$$\frac{dlnK_x}{dP} = \frac{(a + b - c - d)V}{RT}. \tag{84}$$

It is apparent that if $a + b = c + d$, K_x also is independent of P.

The quantitative effect of a change in pressure upon the proportions of the reacting constituents present at equilibrium may be calculated very simply for a dilute gaseous reaction.

We may write equation (31) in the form

$$K_p = \frac{N_C{}^c \times N_D{}^d}{N_A{}^a \times N_B{}^b} \times \frac{P^{(c+d-a-b)}}{N^{(c+d-a-b)}}, \tag{85}$$

where N represents the total number of mols. in the system. Since K_p is *constant, it is clear that when $a + b = c + d$ the second (P/N)* factor of the right hand side of the equation becomes unity, and no change whatever takes place in the relative number of mols. of the reacting constituents with a change in pressure. If, however, $a + b$ is not equal to $c + d$, the P/N factor will differ from unity and a change must occur in the first factor, by reaction between the constituents, in order to satisfy the equation.

Let us consider a system at equilibrium at pressure P_1, for which the numerical values of N_C, N_D, N_A, N_B, etc., have been determined. Let us now change the pressure to P_2. Let x represent the decrease (which might actually be an increase) in the number of mols. of A after equilibrium has been reestablished.

Substituting the new values in equation (85), we have

$$K_p = \frac{\left(N_C + \frac{cx}{a}\right)^c \left(N_D + \frac{dx}{a}\right)^d \cdots}{(N_A - x)^a \left(N_B - \frac{bx}{a}\right)^b \cdots} \times \frac{P_2^{(c+d-a-b)}}{\left(N_1 - \frac{(c+d-a-b)x}{a}\right)^{(c+d-a-b)}}. \tag{86}$$

Since all of the quantities in the equation except x are known, the value of x, and hence the extent of the shift of equilibrium, may be readily calculated.

The effect of pressure upon equilibrium in the liquid phase is ordinarily negligible for moderate changes in pressure. For very considerable pressure changes, however, it may become quite appreciable. The magnitude of the effect, in the case of a perfect solution, may be shown from the following consideration.

If the reaction

$$aA + bB \cdots = cC + dD \cdots \tag{87}$$

occurs at unit pressure P_1, the free energy increase is given by the equation (compare equation (53))

$$\Delta F_1 = cF_{1_C} + dF_{1_D} - aF_{1_A} - bF_{1_B} = RTln\frac{a_C{}^c \times a_D{}^d \cdots}{a_A{}^a \times a_B{}^b \cdots} - RTlnK_a. \tag{88}$$

Since at unit pressure the activity of a perfect solution is equal to its mol. fraction, we may write $a = x$, and equation (88) becomes

$$\Delta F_1 = RTln\frac{X_{1_C}{}^c \times X_{1_D}{}^d \cdots}{X_{1_A}{}^a \times X_{1_B}{}^b \cdots} - RTlnK_{1_x}. \tag{89}$$

If instead of carrying out the reaction at pressure P_1 we raise the pressure to P_2, the molal free energies of each constituent will be increased according to the equation (Chap. II)

$$F_2 = F_1 + \int_{P_1}^{P_2} VdP. \tag{90}$$

The free energy increase of the reaction at pressure P_2 is given, therefore, by the equation

$$\begin{aligned}\Delta F_2 = {} & -aF_{1_A} - bF_{1_B} + cF_{1_C} + dF_{1_D} - a\int_{P_1}^{P_2} V_A dP \\ & - b\int_{P_1}^{P_2} V_B dP + c\int_{P_1}^{P_2} V_C dP + d\int_{P_1}^{P_2} V_D dP.\end{aligned} \tag{91}$$

Combining (89) and (91), we have

$$\begin{aligned}\Delta F_2 = {} & -RTlnK_{1_x} + RTln\frac{X_{1_C}{}^c \times X_{1_D}{}^d}{X_{1_A}{}^a \times X_{1_B}{}^b} - a\int_{P_1}^{P_2} V_A dP \\ & - b\int_{P_1}^{P_2} V_B dP + c\int_{P_1}^{P_2} V_C dP + d\int_{P_1}^{P_2} V_D dP.\end{aligned} \tag{92}$$

Now the free energy increase, ΔF_2, can also be determined by carrying out the reaction through an isothermal reversible process at pressure P_2, similar to that used in deriving equation (53). Each reactant is first changed from its initial mol. fraction (which is still X_1) to the equilibrium value X_2, involving the free energy increase per mol. of $RTln\frac{X_2}{X_1}$, and is then caused to react at the equilibrium condition. The total free energy increase involved in the process is given (equation (53)) by the equation

$$\Delta F_2 = RTln\frac{X_{1_C}{}^c \times X_{1_D}{}^d \cdots}{X_{1_A}{}^a \times X_{1_B}{}^b \cdots} - RTln\frac{X_{2_C}{}^c \times X_{2_D}{}^d \cdots}{X_{2_A}{}^a \times X_{2_B}{}^b \cdots}, \tag{93}$$

where the second member of the right hand side of the equation is evidently K_{2_x}. Equating (92) and (93), we have

$$\begin{aligned}RTlnK_{2_x} - RTlnK_{1_x} = {} & a\int_{P_1}^{P_2} V_A dP + b\int_{P_1}^{P_2} V_B dP \\ & - c\int_{P_1}^{P_2} V_C dP - d\int_{P_1}^{P_2} V_D dP.\end{aligned} \tag{94}$$

If $P_2 - P_1 = dP$, that is, for an infinitesimal change, we may write

$$\frac{dlnK_x}{dP} = \frac{aV_A + bV_B - cV_C - dV_D}{RT}. \tag{95}$$

This equation was first derived by Planck[1] and shows that the rate of change of the equilibrium constant, K_x, with the pressure, is equal to the decrease in the sum of the molal volumes of the reacting substances, divided by RT.

If this equation is compared with that previously derived for a gaseous equilibrium, equation (84), it is apparent that the two become identical when the molal volumes of the constituents are equal to each other, as would be true for dilute gases.

If we consider the relation between K_x and K_c, the mass law constants in terms of the molal concentrations, we may derive an expression for the rate of change of K_c with the pressure.

Thus, from equation (45),

$$K_c = K_x\left(\frac{N}{V}\right)^{(a+b-c-d)}, \tag{96}$$

where N is the total number of mols. (of all kinds) and V the total volume. Taking logarithms,

$$lnK_c = lnK_x + (a + b - c - d)ln\frac{N}{V} \cdot \tag{97}$$

Differentiating, we obtain

$$\frac{dlnK_c}{dP} = \frac{dlnK_x}{dP} - (a + b - c - d)\frac{dln\left(\frac{V}{N}\right)}{dP} \,. \tag{98}$$

If the solution is dilute, we may replace $\frac{V}{N}$ by $\overline{V}$, the molal volume of the solvent, and obtain, using equation (95),

$$\frac{dlnK_c}{dP} = \frac{aV_A + bV_B - cV_C - dV_D}{RT} - (a + b - c - d)\frac{1}{\overline{V}}\frac{d\overline{V}}{dP} \cdot \tag{99}$$

The increase in the partial molal free energy of the solvent with the pressure is given by the equation

$$d\overline{F} = \overline{V}dP. \tag{100}$$

Now, in the chemical reaction in question the increase in the partial molal free energy of the solvent is also given by the equation

$$d\overline{F} = RTln\frac{X_2}{X_1}, \tag{101}$$

where X_1 and X_2 are the mol. fractions of *solvent* before and after the change; i.e.,

$$X_1 = \frac{N_s - a - b}{N} \quad \text{and} \quad X_2 = \frac{N_s - c - d}{N} \,.$$

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[1] Thermodynamics, English Translation, p. 232 (1903), Longmans, Green and Co.

If the solution is quite dilute, $a + b$ and $c + d$ are small as compared with N_s, and, expanding equation (101) by McLaurin's theorem and neglecting higher powers, we obtain

$$d\bar{F} = RT\frac{(c + d - a - b)}{N_s}. \tag{102}$$

Combining equations (102) and (100),

$$\bar{V} = \frac{RT(c + d - a - b)}{NdP}. \tag{103}$$

Substituting this value for $\bar{V}$ in equation (99), we obtain

$$\frac{dlnK_c}{dP} = \frac{aV_A + bV_B - cV_C - dV_D}{RT} + \frac{Nd\bar{V}}{RT}, \tag{104}$$

or, since $(aV_A + bV_B - cV_C - dV_D + Nd\bar{V})$ is equal to the total decrease in volume, $-\Delta V$, which occurs when the reaction takes place,

$$\frac{dlnK_c}{dP} = -\frac{\Delta V}{RT}. \tag{105}$$

This equation has been recently obtained by Rice[1] and by Williams,[2] employing a cyclic process involving the osmotic work produced by concentration changes.

The equation has been tested experimentally by Fanjung,[3] who measured the dissociation of weak organic acids at high pressures.

The Effect of Dilution at Constant Pressure: The effect of volume change upon a chemical equilibrium is more readily seen if we rearrange somewhat the fundamental mass law expressions. Thus we may write equation (31)

$$K_p = \frac{N_C{}^c \times N_D{}^d}{N_A{}^a \times N_B{}^b} \times \frac{P^{(c+d-a-b)}}{(N_A + N_B + N_C + N_D)^{(c+d-a-b)}} \tag{106}$$

and equation (35)

$$K_c = \frac{N_C{}^c \times N_D{}^d}{N_A{}^a \times N_B{}^b} \times V^{(a+b-c-d)}. \tag{107}$$

The effect of dilution of the equilibrium system at constant pressure may now be considered. If the diluent is a substance which does not participate in the chemical reaction, its effect, in general, is only to increase the total number of molecules $(N_A + N_B + N_C + N_D + \cdots)$, and hence the volume. If $a + b = c + d$, it is obvious that the equilibrium is unchanged by such addition, because in such cases the "total number of molecules" factor and the volume factor become unity. If $(a + b)$ is greater than $(c + d)$, the equilibrium must shift with increasing volume in the direction expressed by the equation for the reaction, from left to right, until the new values of N_A, N_B, etc., satisfy equations (106) and (107). If $(a + b)$ is less than $(c + d)$, the reverse change must occur.

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[1] *Trans. Farad. Soc.*, **12**, 318 (1917).

[2] *Trans. Farad. Soc.*, **16**, 458 (1921).

[3] *Z. physik. Chem.*, **14**, 673 (1894).

If the dilution is made with one of the reacting constituents, at constant pressure, the effect on the reaction is not so simply predictable, qualitatively, but is always calculable quantitatively from equation (106) and (107) when the values of N_A, N_B, etc., are known for the particular case.

In this connection it is of interest to consider the proportions in which the reactants for any given reaction should be employed in order to give, at equilibrium, a maximum yield of resultants.

Let us write the reaction

$$aA + bB + cC \cdots = dD + eE + fF \cdots. \tag{108}$$

Let X be the mol. fraction of D present at equilibrium. Then, if no D, E, or F was present at the beginning of the reaction, we have

$$\frac{eX}{d} = \text{the mol. fraction of } E \text{ at equilibrium,}$$

$$\frac{fX}{d} = \text{the mol. fraction of } F \text{ at equilibrium.}$$

Let $r_B, r_C \cdots$ represent the ratio of the mol. fractions of B, C, etc., at equilibrium to the mol. fraction of A. Since the sum of the mol. fractions must be unity, we have

$$X_A + r_B X_A + r_C X_A \cdots + X\left(\frac{d + e + f}{d}\right) = 1. \tag{109}$$

If we denote the term $\left(\frac{d + e + f}{d}\right)$ by m, we have for the various mol. fractions

$$X_A = \frac{1 - mX}{1 + r_B + r_C \cdots},$$

$$X_B = \frac{r_B(1 - mX)}{1 + r_B + r_C \cdots},$$

$$X_C = \frac{r_C(1 - mX)}{1 + r_B + r_C \cdots}.$$

Writing the equation for the mass law at constant temperature and pressure, and substituting the values given above, we have

$$K_x = \frac{X^d \times \left(\frac{eX}{d}\right)^e \times \left(\frac{fX}{d}\right)^f \cdots}{\left(\frac{1 - mX}{1 + r_B + r_C \cdots}\right)^a \times \left(\frac{r_B(1 - mX)}{1 + r_B + r_C \cdots}\right)^b \times \left(\frac{r_C(1 - mX)}{1 + r_B + r_C \cdots}\right)^c \cdots} \qquad (110)$$

or, simplifying,

$$K_x = \frac{X^{(d+e+f)} \frac{d^d \times e^e \times f^f}{d^{(d+e+f)}}}{\left(\frac{1 - mX}{1 + r_B + r_C}\right)^{(a+b+c)} \times r_B{}^b \times r_C{}^c}. \qquad (111)$$

If we denote the two constant factors in the numerator by l and n, we have

$$\frac{nX^l}{(1 - mX)^{(a+b+c)}} = K_x \frac{r_B{}^b \times r_C{}^c \cdots}{(1 + r_B + r_C \cdots)^{(a+b+c)}}. \qquad (112)$$

By applying the principles of the differential calculus, it may be shown that X is a maximum when $r_B = \frac{b}{a}$; $r_C = \frac{c}{a}$; or when

$$\frac{X_A}{a} = \frac{X_B}{b} = \frac{X_C}{c} \cdots.$$

This can, however, only be the case when the same proportions held in the original mixture or, in other words, when the original mixture contained the reactants in the proportions which are required by the chemical equation. As an illustration, in the reaction

$$N_2 + 3H_2 = 2NH_3,$$

the maximum percentage of NH_3 that can be in equilibrium with a mixture of N_2 and H_2 at any given pressure and temperature is produced by bringing to equilibrium a mixture of N_2 and H_2 in the molal ratio of 1 : 3.

The effect of the addition to the equilibrium mixture of indifferent or reacting substances at constant volume is clear from consideration of equation (107). Thus, an indifferent substance will not be expected to change in any way an equilibrium at constant volume (except as indicated below), and the effect of an addition of one of the reacting constituents will be to displace the equilibrium in such a way as to decrease the number of mols. of the other constituents on the side of the chemical equation which includes the substance added, and to increase the number of mols. of the substances on the opposite side of the equation.

In considering the effect upon a system in equilibrium, we have considered the addition of substances not participating in the reaction as merely increasing the total number of molecules. This assumes, however, that the activities of the reacting species are still equal to their mol. fractions or to their partial pressures. If the added substance affects this relationship, it will be expected to have a specific influence on the equilibrium concentrations. For dilute gases in general, the addition of an indifferent gas does not affect the other gases measurably, but with gases at high pressures, and in the case of liquid solutions, the effect of adding "indifferent" substances may not be predicted simply from the volume change. With many organic compounds, the activity may be approximately given by the mol. fraction over a wide range of concentrations, but, in the case of other substances, particularly strong electrolytes, the activities of the reacting species may be markedly affected by the addition of apparently indifferent substances, and the equilibrium concentrations may change accordingly.

The special case involving the addition of a catalyst is discussed further below and the effect of a solvent in liquid systems will be treated in a later section.

Catalysts and Equilibrium: In the experimental measurement of equilibrium it very frequently happens that the rate of the reaction is not sufficient to bring about the condition of equilibrium in a reasonable time at the temperature at which it is desired to operate. In such cases it is usual to resort to the use of various substances which accelerate the *rate* of the reaction without apparently affecting the equilibrium. As the literature contains frequent statements that "a catalyst cannot affect the equilibrium" and occasional objections to this view, it may be well to consider the subject in some detail.

The general law of mass action, equation (30), was derived from consideration of the initial and final states of the system, and must be independent of the mechanism by which the change takes place. It follows, therefore, that the activity constant, K_a, and the free energy change for the reaction must be unaffected by the presence of any substance occurring on both sides of the chemical equation, provided the equation is otherwise unchanged. Thus, if a mixture of nitrogen and hydrogen is passed over a solid catalyst so slowly that equilibrium is obtained, the partial pressure of N_2, H_2 and NH_3 in the issuing gas will be necessarily the same as those which would have been present had the equilibrium been produced in the absence of a catalyst. In all cases of this type it is quite clear that the catalyst does not affect the equilibrium. Nevertheless it is quite possible for a catalyst to affect the equilibrium *concentrations* for a given reaction, if it is present in such quantity as to affect the activity of one or more of the reacting species. Thus, strong mineral acids are known to accelerate the reaction between alcohols and organic acids, and also the hydrolysis of the corresponding esters, and acids have been used as catalysts to facilitate the measurement of equilibrium in such reactions. The mol. fractions of ester, alcohol, acid and water may, however, have in such cases appreciably different values from those obtained without the use of a catalyst, for the mineral acid affects the *activity of the water* (and probably, to a lesser extent, the other constituents), so that the activity of the water is no longer equal to its mol. fraction. This effect is particularly apt to occur in equilibria which involve electrolytes, either as reactants or as catalysts, and must be taken into consideration in measurements of equilibrium.

Thus, in measurements in which the catalyst is actually present in the system when the equilibrium is measured, the possibility must be considered that it may have an effect upon the activity of the reacting species, and thus lead to erroneous values for the equilibrium constant and the free energy change. This is, of course, also true of any "indifferent" molecular species which may be present in the system, as indicated above.

The difficulties which have arisen in considering the effect or lack of effect of a catalyst upon equilibrium have usually arisen from failure to consider carefully the assumptions underlying the particular equilibrium expressions which may have been employed.

In general, there is no serious difficulty in determining experimentally the question of the possible influence of the catalyst upon the equilibrium.

MEASUREMENT OF CHEMICAL EQUILIBRIUM

The experimental measurement of chemical equilibrium frequently presents problems of considerable difficulty. The position of equilibrium may be such that the reaction goes nearly to completion in one direction, and the concentrations of one or more of the reacting species may become immeasurably small. In other cases, the rate of the reaction may be so slow that equilibrium is not established in any convenient time at the temperature at which it is desired to measure it. Again, the rate of reaction may be so rapid that an attempt to analyze the equilibrium mixture results in a shift of the equilibrium. In the reactions of organic chemistry, and in many inorganic reactions, the problem is complicated by the occurrence of other reactions than the one whose equilibrium it is desired to measure. No general procedure can be indicated for the determination of the condition of equilibrium, as each problem is apt to require individual treatment; a few types of experimental method which have been used successfully may, however, be noted. The first step, in general, consists in determining that the reaction proceeds in each direction at some definite temperature, at a rate sufficiently rapid to permit the establishment of equilibrium within a reasonable time. The rate at a given temperature may frequently be increased by the selection of a suitable catalyst, which should not affect the equilibrium (see, however, the preceding section). Known proportions of the reacting substances are then brought in contact and are kept at the temperature in question until the mixture does not change in composition with increased time.

The analysis of the mixture must then be carried out in such a way as to prevent appreciable change in the composition by reaction during the time necessary for the analysis. Similar determinations should be made in which the equilibrium is approached from the opposite side, and experiments in which the initial proportions of reactants are varied are usually necessary in order to calculate definitely an equilibrium "constant" for the reaction.

If possible, the analysis of the mixture is made at the temperature of the measurement of the equilibrium, by the determination of some physical property whose change can be shown to be proportional to the extent of reaction. Thus, the density may measure the extent of a reaction between gases in which the total number of molecules changes with the reaction; color, refractive index, optical rotation, etc., may in individual cases serve to measure the equilibrium concentrations.

If the analysis cannot be made without disturbing the system, recourse may be had to the procedure of lowering the temperature of the mixture very rapidly to some temperature so low that the rate of reaction is inappreciable in the time necessary for an analysis. The feasibility of this process will vary with the individual case.

In the case of reactions between gases, which are apt to occur with considerable velocity only at the surface of solid catalysts, dynamic methods are frequently employed, the reacting mixture being passed over the catalyst so slowly that further decrease in the rate of flow does not produce further change in composition (thus indicating the existence of equilibrium), and the gas issuing from the catalyst is cooled and analyzed. Since the rate of the reaction in the absence of the catalyst is frequently negligible, it is thus possible to maintain the mixture unchanged from the equilibrium condition for considerable periods of time.

In a great many cases in which it has not been found possible to measure the equilibrium of a chemical reaction directly because of experimental difficulties, it becomes possible to calculate it indirectly from a determination of the equilibria for reactions which, when combined, will give the reaction in question. Thus, consider the reactions

$$H_2 + \tfrac{1}{2}O_2 = H_2O, \tag{113}$$

$$CO + \tfrac{1}{2}O_2 = CO_2, \tag{114}$$

$$CO + H_2O = CO_2 + H_2, \tag{115}$$

for which at high temperatures and moderate pressures we may write

$$K_p' = \frac{P_{H_2O}}{P_{H_2} \times P_{O_2}^{1/2}}, \tag{116}$$

$$K_p'' = \frac{P_{CO_2}}{P_{CO} \times P_{O_2}^{1/2}}, \tag{117}$$

$$K_p''' = \frac{P_{CO_2} \times P_{H_2}}{P_{CO} \times P_{H_2O}}. \tag{118}$$

Each of these equations represents the relation which must exist at equilibrium between the partial pressures of the reacting constituents, regardless of any other substances which may be present. In a system at equilibrium containing both H_2O and CO_2, CO, H_2 and O_2 must also be present, and the partial pressures of the different constituents must adjust themselves in such a way that all three equations are satisfied. Obviously, then, equations (116), (117) and (118) are properly to be regarded as simultaneous equations, and if any two are known the third may be calculated. Thus, it might be that the dissociation of water could not be measured at a given temperature; while that of CO_2 (117) and the equilibrium of the water gas reaction (118) were experimentally measurable. The dissociation constant for H_2O is then calculable without direct measurement.

This principle is of the utmost importance, and its use has permitted the calculation of the equilibrium of numerous important reactions.

Furthermore, the equilibrium constant is directly related to the free energy of reaction (p. 305) which is frequently calculable from such data as the electromotive force of cells (Chap. XII) or from the entropies of the reacting and resulting substances (Chap. XVII). It has sometimes been possible to utilize very elaborate combinations of reactions to calculate the equilibrium constant not directly measurable.[1] It must be remembered, however, that cumulative experimental error is apt to occur if too many different data are combined.

If the approximate condition of equilibrium is known, it is frequently possible to determine the exact condition by preparing a series of mixtures approximating in composition that estimated for the equilibrium, and noting their rate of change, by means of analysis, or by some physical measurement. If it can be shown that one mixture is changing in one direction, and another in the opposite direction, the true equilibrium must lie between these limits, and by repeating the experiments it is possible to make the limits as narrow as is desired. This procedure is frequently employed when complicating reactions are apt to occur if too long a period of time were allowed for the reaction.

Homogeneous Equilibrium in the Gaseous Phase

Most measurements of gaseous equilibrium have been carried out at pressures in the neighborhood of atmospheric, and at somewhat elevated temperatures, so that the activity of each reacting species is approximately equal to its partial pressure. Under these conditions the equilibrium is expressed by equation (31) above.

Reactions in which no Change in the Number of Molecules Occur: If the number of molecules of resultants is equal to that of the reactants, it is apparent from equation (31) that changes in the *total pressure* of the system will be without effect upon the position of equilibrium, so long as the partial pressures of the reacting substances may be considered as approximately equal to their activities. Examples of this type of reaction which have been the subject of extensive experimental investigation are

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[1] See Lewis and Randall, Thermodynamics and Chemistry, 488, 528, 1923.

$$H_2 + I_2 = 2HI \tag{119}$$

and

$$H_2 + CO_2 = CO + H_2O. \tag{120}$$

The former of these reactions was investigated thoroughly by Bodenstein,[1] who allowed known quantities of hydrogen and iodine to react until equilibrium was reached, and then, after sudden cooling, determined the hydriodic acid formed.

If a represents the number of mols. of H_2 taken at the start of the reaction, b the number of mols. of I_2, $2x$ the number of mols. of HI formed after equilibrium has been reached, and P the total pressure, we have, for the equilibrium partial pressures,

$$p_{H_2} = \frac{(a - x)P}{a + b},$$

$$p_{I_2} = \frac{(b - x)P}{a + b},$$

$$p_{HI} = \frac{(2x)P}{a + b},$$

whence

$$K_p = \frac{p_{HI}^2}{p_{H_2} \times p_{I_2}} = \frac{4x^2}{(a - x)(b - x)}. \tag{121}$$

In Table I are given characteristic experimental data obtained by Bodenstein, and also values of x calculated from equation (121), taking the value of K as 50.4, the mean experimental value at 454°. The close agreement shows that equation (121) represents quite closely the experimental facts of this equilibrium.

TABLE I

EQUILIBRIUM DATA, $H_2 + I_2 = 2HI$
Temperature = 454°; K_p = 50.4

H_2 at Start cc. (a)	I_2 at Start cc. (b)	HI Formed cc. ($2x$)	HI Calc. from Eq. (121) ($2x$)
8.10	2.94	5.64	5.66
7.94	5.30	9.49	9.52
8.07	9.27	13.47	13.34
8.12	14.44	14.93	14.82
8.02	27.53	15.54	15.40
7.89	33.10	15.40	15.12

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[1] *Z. physik. Chem.*, 29, 295 (1899).

The reaction

$$H_2 + CO_2 = CO + H_2O$$

has been studied very extensively, as it is of technical importance both in the manufacture of "water gas" and in the manufacture of hydrogen from water gas. The most important data are those of Hahn[1] and of Haber and Richardt[2] whose investigations combined cover the temperature range of about 600° C. to 1500° C.

The experimental method of Hahn consisted in allowing a slow stream of gases, of known composition, to pass over a catalyst, and in then cooling the gases rapidly and analyzing them. Characteristic data taken for the temperature of 980° C. are given in Table II and illustrate very well the relation existing between the partial pressures of the reacting gases at equilibrium. In these particular experiments the initial gases were mixtures of CO_2 and H_2 in varying proportions, and therefore in the equilibrium mixture the CO and H_2O are of equal volume percentage. The values of K_p calculated from the equation

$$K_p = \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}} \tag{122}$$

show only irregular variations from the mean of 1.60.

The effect of temperature upon the equilibrium was investigated by both Haber and Hahn and their data have been recalculated by both Haber[3] and by Lewis and Randall.[4]

The latter authors have shown that the variation of the equilibrium constant with the temperature is well represented by an equation of the form of equation (79).

Their equation is

$$lnK_p = -\frac{10,100}{RT} + \frac{1.81 lnT}{R} - \frac{0.00445T}{R} + \frac{0.00000068T^2}{R} + 0.272. \tag{123}$$

Values of K_p calculated from equation (123) show a rapid change in the values of the equilibrium constant with the temperature, the equilibrium being displaced largely toward the right at high temperatures, and to the left at low temperatures. In the technical preparation of hydrogen by means of this reaction, the starting point is usually a mixture of CO and H_2 in approximately equivalent proportions. It is desired to obtain from it a mixture as low in CO and as high in H_2 as possible. From considerations of equations (122) and (123) it is clear that this result may be achieved by operating at as low a temperature as possible, and by adding steam (which may later be removed readily) to the mixed gases. The limits to which these procedures may be effective commercially are determined by the rate of reaction at low temperatures, by the cost of steam, etc.[1]

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[1] *Z. physik. Chem.*, **44**, 513 (1904); **48**, 735 (1904).

[2] *Z. anorg. Chem.*, **38**, 5 (1904).

[3] Haber, Thermodynamics of Technical Gas Reactions (tr.), Longmans, Green & Co., 1908.

[4] Lewis and Randall, Thermodynamics and Chemistry, McGraw Hill Co., 1923, p. 574.

TABLE II

EQUILIBRIUM DATA IN WATER GAS REACTION
Temperature = 986° C.

Initial Composition Per Cent by Volume		Equilibrium Composition Per Cent by Volume		
CO_2	H_2	CO_2	$CO = H_2O$	H_2
10.1	89.9	0.70	9.46	80.38
		0.67	9.33	80.67
30.1	69.9	7.18	23.00	46 82
		7.12	22.92	47.04
49.1	51.9	21.52	27.83	22.82
		20.78	28.04	23.14
		21.36	27.88	22.87
60.9	39.1	34.67	26.25	12.77
		34.20	26.61	12.58
70.3	29.7	47.66	22.79	6.76
		47.35	22.85	6.95

Another reaction of this class, which is of industrial importance, is that between nitrogen and oxygen, in accordance with the equation

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 = NO. \qquad (124)$$

The rate at which equilibrium is established for the reaction is extremely slow and it has been measured directly only at temperatures of 1500° C. and above.[2] Even at these temperatures the percentage of nitric oxide produced by heating air until equilibrium is established is extremely small, being 0.377 at 1540° C. and 2.33 at 2400° C. At any given temperature the per cent of nitric oxide in equilibrium could be increased somewhat by heating a 1 : 1 mixture of N_2 and O_2 (compare p. 316), but, in the technical utilization of the reaction for the fixation of nitrogen, the increased percentage of nitric oxide would not be sufficient to warrant the use of artificial $N_2 : O_2$ mixture instead of air. The variation of the equilibrium constant with the temperature is expressed by the equation

$$lnK_p = -\frac{21,600}{RT} + \frac{2.50}{R} \cdot \qquad (125)$$

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[1] For a discussion of the technical problem the reader is referred to Taylor, Industrial Hydrogen, Chemical Catalog Co., 1921. Later data on the water-gas equilibrium are to be found in *J. Am. Chem. Soc.*, **46**, 888 (1924).

[2] Nernst, *Z. anorg. Chem.*, **49**, 213 (1906).

Since the heat capacities of nitrogen and oxygen are identical with that of nitric oxide, the heat of the reaction does not vary with the temperature, and the characteristic equation assumes the simple form given above.

Reactions in which the Total Number of Molecules Changes: A great number of gas reactions of this type have been the subject of experimental investigation. In illustration may be cited the following:

$$CO + \tfrac{1}{2}O_2 = CO_2, \tag{126}$$ [1]

$$H_2 + \tfrac{1}{2}O_2 = H_2O, \tag{127}$$ [2]

$$N_2O_4 = 2NO_2, \tag{128}$$ [3]

$$NO_2 = NO + \tfrac{1}{2}O_2, \tag{129}$$ [4]

$$I_2 = 2I, \tag{130}$$ [5]

$$(CH_3COOH)_2 = 2CH_3COOH, \tag{131}$$ [6]

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3, \tag{132}$$ [7]

$$SO_2 + \tfrac{1}{2}O_2 = SO_3, \tag{133}$$ [8]

$$HCl + \tfrac{1}{4}O_2 = \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2O. \tag{134}$$ [9]

Certain of these reactions will be discussed in some detail to illustrate experimental method and to point out the applications of the equilibrium laws to practical problems.

When the equation is so written as to indicate the breaking up of a single molecular species into either more than one molecule of an individual substance (equations (128), (130) and (131)) or into more than one kind of molecule (equations (129) and (126), (127), (132) and (133) written in the opposite sense), the reaction is frequently termed a *dissociation*, and the equilibrium constant is called the dissociation constant. In examining values for equilibrium constants occurring in the literature, care should always be taken to

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(These references are not complete, they refer to the more important investigations.)

[1] Nernst and von Wartenburg, *Z. physik Chem*, **56**, 548 (1906).
Langmuir, *J. Am. Chem. Soc.*, **28**, 1357 (1906).
Lowenstein, *Z. physik. Chem.*, **54**, 797 (1905).

[2] Nernst and von Wartenburg, *Nacht. Kgl ges Wiss.*, Gottingen (1905).
Lowenstein, *Z. physik. Chem.*, **56**, 513 (1906).
Langmuir, *J. Am. Chem. Soc.*, **28**, 1357 (1906).

[3] Schreber, *Z. physik. Chem.*, **24**, 651 (1897).
Bodenstein and Katayama, *Z. Elektrochem*, **15**, 244 (1909).
Bodenstein, *Z. anorg. Chem*, **100**, 68 (1922).

[4] Bodenstein and Katayama (*loc. cit.*), Bodenstein (*loc. cit.*).

[5] Stark and Bodenstein, *Z. Elektrochem.*, **16**, 961 (1910).

[6] Drucker and Ullmann, *Z. physik. Chem.*, **74**, 567 (1910).

[7] Haber, *Z. Elektrochem.*, **20**, 592 (1914).
Haber, Tamaru and Ponnay, *Z. Elektrochem*, **21**, 89 (1915).
Haber and Maschke, *Z. Elektrochem.*, **21**, 129 (1915).
Haber and Greenwood, *Z. Elektrochem.*, **21**, 241 (1915).
Larson and Dodge, *J. Am. Chem. Soc*, **45**, 2918 (1923).
Larson, *J. Am. Chem. Soc.*, **46**, 367 (1924).

[8] Bodenstein and Pohl, *Z. Elektrochem.*, **11**, 373 (1905).

[9] Lunge and Marmier, *Z. angew. Chem.*, **10**, 105 (1897).
Lewis, *J. Am. Chem. Soc.*, **28**, 1380 (1906).
von Falkenstein, *Z. physik. Chem.*, **59**, 313 (1907).

note the direction in which the reaction is written, and also the exact equilibrium constant employed, for the numerical values of K_p, K_c and K_x are not identical for reactions in which the number of molecules changes, as previously shown.

Dissociation of Carbon Dioxide: The reaction

$$CO + \tfrac{1}{2}O_2 = CO_2 \tag{135}$$

goes ordinarily so nearly to completion from left to right that direct measurement of the equilibrium constant represents a difficult experimental problem. Nevertheless, very satisfactory data have been obtained by Nernst and his students. Nernst and von Wartenburg passed carbon dioxide through a heated tube and then, after rapid cooling, analyzed the gases formed; Langmuir passed carbon dioxide either alone or mixed with carbon monoxide or oxygen, around a heated platinum wire at high velocity, and analyzed the issuing gases; Lowenstein made use of the Victor Meyer apparatus. Their measurements cover the range of 1100° C. to 1450° C. Pure carbon dioxide is dissociated at atmospheric pressure to the extent of only 0.4 per cent at the highest temperature measured, and is only 0.0142 per cent dissociated at 1100° C.

These data are in very good agreement with calculations of the equilibrium made indirectly by combination of other data.

The equation[1]

$$lnK_p = \frac{67{,}510}{RT} - \frac{2.75lnT}{R} + \frac{0.0028T}{R} + \frac{0.00000031T^2}{R} - \frac{4.46}{R} \tag{136}$$

expresses quite accurately the variation of the equilibrium constant with the temperature.

The dissociation of carbon dioxide will vary with the total pressure, as shown in an earlier section. If a represents the fraction of carbon dioxide dissociated, then we may write the mass law equation

$$K_p = \frac{P_{CO_2}}{P_{CO} \times P_{O_2}^{1/2}} = \frac{(1-a)P}{aP(0.5aP)^{1/2}} = \frac{\sqrt{2}(1-a)}{a^{3/2} \times P^{1/2}} \cdot \tag{137}$$

For values for which a is small as compared with unity, we may write this equation

$$a = \frac{K}{P^{1/3}} \cdot \tag{138}$$

The dissociation varies, then, inversely with the 1/3 power of the total pressure.

Dissociation of Water Vapor: The reaction

$$H_2 + \tfrac{1}{2}O_2 = H_2O \tag{139}$$

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[1] Lewis and Randall, Thermodynamics and Chemistry, McGraw Hill Co. (1923).

proceeds even more nearly to completion than reaction (135), but its equilibrium has been measured by the same methods and the same investigators as those cited in the preceding case. In addition, Lowenstein, making use of the fact that hydrogen gas passes readily through hot platinum, measured directly the partial pressure of hydrogen in equilibrium with water vapor and oxygen. The data show that water vapor is dissociated at atmospheric pressure to less than 0.01 per cent at 1100° C. and the dissociation has risen to only 1.8 per cent at 2000° C.

This important reaction has been the subject of many indirect measurements and the data from all sources agree admirably with the equation

$$lnK_p = \frac{57{,}410}{RT} - \frac{0.94 lnT}{R} - \frac{0.001657T}{R} + \frac{0.00000037T^2}{R} - \frac{3.92}{R}. \qquad (140)$$

The Dissociation of Nitrogen Tetroxide: Nitrogen tetroxide is appreciably dissociated at 0° C.,

$$N_2O_4 = 2NO_2, \qquad (141)$$

and the amount of dissociation increases rapidly with increasing temperature. The experimental measurement of the equilibrium conditions has thus been very simple, and, as a result, the literature contains many references to the reaction. The measurements have usually involved the determination of the density of the gas, and, as the method is one of the most frequently used in studying equilibria in gas reactions in which the total number of molecules changes, it may be considered in some detail.

The density (gm./liter) of any gas which obeys the gas laws is given by the equation

$$d_t = \frac{MP}{RT}, \qquad (142)$$

where M is the molecular weight and P the total pressure. This density we may call the theoretical density, d_t. If dissociation occurs, the volume will increase in proportion to the increase in the total number of molecules, and since the total weight remains constant, the density will decrease in the same proportion. In the case of one mol. N_2O_4, if a is the fraction dissociated, $1 - a$ will be the number of mols. of undissociated gas, and $2a$ will be the number of mols. of NO_2. The total number of mols. will be $1 + a$, and the observed density will bear the relation to the theoretical density

$$\frac{d_0}{d_t} = \frac{1}{1 + a}. \qquad (143)$$

Rearranging, we have

$$a = \frac{d_t - d_0}{d_0}. \qquad (144)$$

The dissociation constant K_p is given by the equation

$$K_p = \frac{p_{NO_2}{}^2}{p_{N_2O_4}} = \frac{\left(\dfrac{a}{1+a}P\right)^2}{\left(\dfrac{1-a}{1+a}\right)P} = \frac{a^2P}{(1-a^2)}. \tag{145}$$

In this case the dissociation (a) varies, when the dissociation is small, inversely as the square root of the pressure.

It should be noted that if a substance dissociates into N molecules instead of 2 as in the case above, equation (144) becomes

$$a = \frac{d_t - d_0}{(N-1)d_0}. \tag{146}$$

The values of K_p for the dissociation are 0.0154 at 0° C. and 13.33 at 100° C.; the variation with the temperature for this range is given by the equation

$$lnK_p = -\frac{13{,}600}{RT} + \frac{41.6}{R}. \tag{147}$$

The Dissociation of Nitrogen Dioxide: At temperatures of 150° C. and more, nitrogen dioxide begins to be measurably dissociated into nitric oxide and oxygen, the reaction occurring according to equation (148),

$$NO_2 = NO + \tfrac{1}{2}O_2. \tag{148}$$

The value of the equilibrium constant is of some technical importance, as the reverse reaction occurs at one stage in the preparation of nitric acid from nitric oxide, formed either by oxidation of atmospheric nitrogen (see p. 324) or by oxidation of ammonia. The equilibrium constant has been measured by Bodenstein and Katayama (*loc. cit.*), and later by Bodenstein (*loc. cit.*), from careful determinations of the density of the reaction mixture. The temperature range in the latter work was 220° C. to 550° C. Above 550° C., the measurements were made uncertain by partial decomposition of the nitric oxide into nitrogen and oxygen. The data of Bodenstein are well represented by the empirical equation

$$lnK_p = -\frac{5749}{T} + 1.75\,lnT - 0.000507T + 2.839. \tag{149}$$

The equation employed by Lewis and Randall is

$$lnK_p = -\frac{14{,}170}{RT} + \frac{2.75lnT}{R} - \frac{0.0028T}{R} + \frac{0.00000031T^2}{R} + \frac{2.73}{R}. \tag{150}$$

The Ammonia Equilibrium: This reaction has received a large amount of attention because of its great importance for the commercial synthesis of ammonia,

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3. \tag{151}$$

The success which has attended this industry is a striking example of the value of the application of principles of physical chemistry to a technical problem. At first sight, the reaction would appear to be impossible as a source of commercial ammonia, for nitrogen and hydrogen do not combine at measurable rates at low temperatures. At temperatures at which the rate of reaction is appreciable, the percentage of ammonia at equilibrium at atmospheric pressure is inappreciable.

If we write the equation

$$K_p = \frac{p_{NH_3}}{p_{H_2}^{3/2} \times p_{N_2}^{1/2}}, \tag{152}$$

it is clear that the partial pressure of the ammonia at equilibrium will be increased by increasing the total pressure. This is brought out by considering the special case in which hydrogen and nitrogen are present in the ratio of 1 : 3 (which gives the maximum per cent of NH_3 possible at any given temperature and pressure, as shown in a preceding section. If the volume fraction of ammonia present in the gas at equilibrium is denoted by a, and if P is the total pressure, we may write equation (152) [1]

$$\frac{a}{(1 - a)^2} = KP. \tag{153}$$

When a is small compared with unity, it varies almost directly with the total pressure. By operating at pressures of 30 atmospheres, Haber and his students (*loc. cit.*) were able to determine values of the equilibrium constant with considerable accuracy. Recent investigations by Larson, and Larson and Dodge (*loc. cit.*), have included measurements of the equilibrium constant up to 1000 atmospheres pressure, under conditions in which the gas laws no longer hold. These data are discussed further below.

The variation of the equilibrium constant with the temperature may be expressed with fair accuracy by a simple equation, suggested by Haber, namely,

$$lnK_p = \frac{13{,}200}{RT} - 6.134. \tag{154}$$

From the data of Haber, and from consideration of the heat capacities of the reacting gases, Lewis and Randall (*loc. cit.*) propose the equation

$$lnK_p = \frac{9500}{RT} - \frac{4.96lnT}{R} - \frac{0.000575T}{R} + \frac{0.000000085T^2}{R} + \frac{9.61}{R}. \tag{155}$$

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[1] Tour, *J. Ind. Eng. Chem.*, **13**, 298 (1921).

Larson and Dodge have also proposed empirical equations representing their own data at different pressures. Obviously, low temperatures and high pressure increase rapidly the proportion of ammonia at equilibrium, and the success of the industry of ammonia synthesis has been achieved by the development of catalysts which permit moderate temperatures of operation, and of apparatus for carrying out the reaction between 100 and 1000 atmospheres pressure.

The Oxidation of Sulphur Dioxide: The equilibrium in this reaction

$$SO_2 + \tfrac{1}{2}O_2 = SO_3 \tag{156}$$

has been the subject of many careful investigations, particularly because of its bearing upon the "contact" process for the manufacture of sulfuric acid. The experimental method has usually consisted in passing a mixture of sulfur dioxide and oxygen, alone or mixed with nitrogen, over a catalyst of finely divided platinum, and then analyzing the gases after rapid cooling. The earlier investigations of Knietsch[1] have been superseded by the more accurate work of Bodenstein and Pohl (*loc. cit.*), who carried out very careful determinations of the equilibrium with various mixtures of sulphur dioxide, oxygen and nitrogen, over a range of temperature of about 500° C. to 800° C. Their data show that the equilibrium constant corresponds to that required by the equation

$$K_p = \frac{P_{SO_3}}{P_{SO_2} \times P_{O_2}^{1/2}}, \tag{157}$$

where the variation of K_p with the temperature is expressed by the equation (Lewis and Randall, *loc. cit.*)

$$lnK_p = \frac{22{,}600}{RT} - \frac{21.36}{R}. \tag{158}$$

In technical practice, it is desired to bring about as completely as possible the oxidation of the sulphur dioxide, possible variables being the composition of the mixture, the temperature and the pressure. It is instructive to write equation (157) as follows:

$$\frac{N_{SO_3}}{N_{SO_2}} = K_p \sqrt{\frac{N_{O_2}}{N} \times P}, \tag{159}$$

where N refers to the total number of mols. of gas present, the subscript identifying the individual gases. The term on the left of the equation (159) should have for commercial operation a value of the order of 50–100, which represents 98 to 99 per cent efficiency of oxidation. Obviously, the ratio of SO_3/SO_2 will increase with increase in total pressure, but only proportional to the square root of the total pressure, so that a great gain in efficiency is not to be expected from pressure change. The effect of the excess oxygen N_{O_2}, is also clear from equation (159). If N_{O_2} should be extremely small, it might reduce the efficiency of oxidation considerably, but unless this is the case, changes in N_{O_2}, do not alter appreciably the SO_3/SO_2 ratio; for, an increase in N_{O_2} also increases N, and the SO_3/SO_2 ratio is proportional only to the square root of this ratio. If N_{O_2} is increased by adding *air* (essentially one O_2 to four N_2), the ratio of N_{O_2}/N may be *decreased* instead of increased, and the efficiency of oxidation affected unfavorably. Obviously, therefore, with a moderate excess of oxygen and at moderate pressures, the only way in which a high equilibrium value of the SO_3/SO_2 ratio may be obtained is by operating under temperature conditions for which K_p has a high value. Technically, the reaction is carried out so that the temperature of the gas issuing from the reaction system is about 425° C. to 450° C., where K_p has values of about 200 and 400 respectively.

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[1] Knietsch, *Ber.*, **34**, 4069 (1901); *Ber. V. Int. Kon. Angew. Chem.*, **1**, 617 (1904).

The Oxidation of Hydrogen Chloride: The oxidation of hydrochloric acid gas by oxygen which occurs readily at temperatures around 400° C. in the presence of cupric chloride as a catalyst has become an industry of importance for the commercial preparation of chlorine, by the Deacon process.

$$HCl + \tfrac{1}{4}O_2 = \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2O. \qquad (160)$$

Investigations by Lewis (*loc. cit.*), von Falkenstein (*loc. cit.*), and others have shown that the condition of equilibrium corresponds to that required by the equation

$$K_p = \frac{P^{1/2}_{Cl_2} \times P^{1/2}_{H_2O}}{P_{HCl} \times P^{1/4}_{O_2}}. \qquad (161)$$

In practice, mixtures of hydrochloric acid gas and air are passed over the catalyst, and the undecomposed hydrogen chloride is absorbed by water. In considering the extent to which the hydrochloric acid may be oxidized, it is somewhat convenient to transform equation (161).

If we multiply numerator and denominator by $P^{1/2}_{Cl_2}$, and rearrange, we obtain

$$\frac{P_{Cl_2}}{P_{HCl}} \times \frac{1}{P^{1/4}_{O_2}} \times \frac{P^{1/2}_{H_2O}}{P^{1/2}_{Cl_2}} = K_p. \qquad (162)$$

If we consider 1 mol. of HCl, and if x represents the fraction decomposed, the ratio P_{Cl_2}/P_{HCl} becomes $x/2(1 - x)$. If the initial gas mixture is dry, $P_{Cl_2} = P_{H_2O}$, and equation (162) may be written

$$\frac{x}{(1 - x)} = 2K_p\left(\frac{N_{O_2}}{N}\right)^{1/4} \times P^{1/4}. \qquad (163)$$

The effect upon the efficiency of oxidation of changes in the pressure, and addition of oxygen or air, is clearly shown by this equation.

The variation of K_p with the temperature is calculated by Lewis and Randall to follow the equation

$$lnK_p = \frac{6835}{RT} - \frac{0.02lnT}{R} - \frac{0.00085T^2}{R} + \frac{0.000000185T^2}{R} - \frac{7.27}{R}. \qquad (164)$$

Gaseous Reactions at High Pressures: The equation for the law of mass action (Equation 4) expressing the dynamic nature of equilibrium

$$\frac{K_1}{K_2} = K = \frac{A_C \times A_D}{A_A \times A_B}$$

may obviously be expected to be valid under conditions in which the gas laws are approximately obeyed. If the partial pressure of a gas differs markedly from the activity, it is not to be expected that the "constant" of equation (4) will be strictly independent of the initial proportions of the reacting substances, or of the total pressure. Most equilibria in gaseous systems have been measured at fairly high temperatures and low pressures, where the gas laws are approximately valid for nearly all gases, but at least one equilibrium, that of the technically important reaction

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3, \qquad (164)$$

has been measured at quite high pressures, the recent measurements of Larson and of Larson and Dodge[1] extending the range of experimental data to 1000 atmospheres pressure. It is interesting to consider their data, some of which are given in Table III and Table IV.

TABLE III

PER CENT OF NH_3 IN EQUILIBRIUM WITH A 1 : 3, N_2-H_2 MIXTURE

Temperature ° C.	Pressures in Atmospheres						
	10	30	50	100	300	600	1000
325	10.38						
350	7.35	17.80	25.11				
375	5.25	13.35	19.44	30.95			
400	3.85	10.09	15.11	24.91			
425	2.80	7.59	11.71	20.23			
450	2.04	5 80	9.17	16.36	35.5	53.6	69.4
475	1.61	4.53	7.13	12.98	31.0	47.5	63.5
500	1.20	3.48	5.58	10.40	26.2	42 1	—

The extent of deviation of the reacting gases at the range of pressures and temperatures cannot be predicted from available data on equations of state, but it is reasonable to suppose that the deviation for hydrogen and nitrogen is comparatively small, while that for ammonia may be expected to be much larger. With increasing pressure and decreasing temperature not only will the deviation of all gases be greater but also the proportion of ammonia in the equilibrium mixture will increase. It is, therefore, to be expected that

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[1] *J. Am. Chem. Soc.*, **45**, 2918 (1923); **46**, 367 (1924).

TABLE IV

EQUILIBRIUM CONSTANT

$$K_p = \frac{P_{NH_3}}{P_{N_2}^{1/2} \times P_{H_2}^{3/2}}$$

Temperature ° C.	Pressures in Atmospheres						
	10	30	50	100	300	600	1000
350	0.0266	0.0273	0.0278				
375	0.0181	0.0184	0.0186	0.0202			
400	0.0129	0.0129	0.0130	0.0137			
425	0.00919	0.00919	0.00932	0.00987			
450	0.00659	0.00676	0.00690	0.00725	0.00884	0.01294	0.02328
475	0.00516	0.00515	0.00513	0.00532	0.00674	0.00895	0.01493
500	0.00381	0.00386	0.00388	0.00402	0.00498	0.00651	

the value for K_p will show a greater variation with the pressure at the lower temperature than at the higher temperatures. This is borne out by the data in Table IV, from which it appears that K_p at 375° C increases by about 10 per cent in changing from 10 atmospheres to 100 atmospheres, while at 500° C. the variation is about one-half that value The value at 450° C. at 600 atmospheres is nearly twice that at 10 atmospheres, while at 500° C. the value at 600 atmospheres is about 1.7 times that at 10 atmospheres. The fact that the constant increases with increasing pressure indicates that the ratio of the partial pressure of ammonia to its activity, P_{NH_3} a_{NH_3}, increases more rapidly with the pressure than the corresponding ratios for nitrogen and hydrogen, as would be expected from the known equation of state of ammonia at lower temperatures. The activity constant, K_a, which must be independent of the pressure, is presumably more nearly given by the values of K_p at the lower pressures.

It would be expected that at the very high pressures the values of K_p would also vary somewhat with the proportions of nitrogen, hydrogen and ammonia in the equilibrium mixtures, but, since all of the experiments were carried out on a mixture of nitrogen and hydrogen in the ratio of 1 : 3, the data do not permit this point to be decided.

HOMOGENEOUS EQUILIBRIUM IN THE LIQUID PHASE

One of the first experimental investigations of equilibrium was that of Berthelot and Pèan de St. Gilles (*loc. cit.*) who carried out an extensive study of the reaction between acetic acid and ethyl alcohol, proved it to be reversible, and showed that their equilibrium data could be represented mathematically by the equation

$$K = \frac{\text{mols. ester} \times \text{mols. water}}{\text{mols. acid} \times \text{mols. alcohol}}, \tag{165}$$

which we recognize as identical with equation (38), remembering that the number of mols. of reactants and resultants are equal. Berthelot and Pèan de St. Gilles mixed alcohol and acetic acid in varying proportions in sealed glass tubes, and heated the tubes at temperatures in the neighborhood of 200° C. until no further change in composition was brought about by further heating. They then analyzed the mixtures for acetic acid, and calculated the composition of the entire mixture from this measurement. If a represents the number of mols. of alcohol taken, b the number of mols. of acetic acid, and x the number of mols. of ester (or water) formed, their experiments show that at equilibrium the proportions of all constituents present are quite closely given by the equation

$$K = \frac{x^2}{(a - x)(b - x)}, \tag{166}$$

where K has the numerical value of 4.0. Table I gives the results of a series of experiments, showing the values of x determined experimentally, and those calculated from equation (166). The agreement is probably within the experimental error, and shows that for the system in question under the conditions of measurement, the activity of the reacting species is approximately proportional to the mol. fraction.

TABLE V[1]

Mols. Acetic Acid Taken a	Mols. Alcohol Taken b	Mols. Ester Formed x (Found)	Mols. Ester Calculated x
1.0	0.05	0.05	0.049
1.0	0.18	0.171	0.171
1.0	0.33	0.293	0.301
1.0	0.50	0.414	0.423
1.0	1.00	0.667[2]	0.667
1.0	2.00	0.858	0.850
1.0	8 00	0.966	0.970

Berthelot and Pèan de St. Gilles found the value of the equilibrium constant to be practically independent of the temperature, a fact confirmed by later investigators,[3] and in accord with the known fact that the heat of reaction must be very close to zero, as shown indirectly by consideration of the heats of combustion of alcohol, acetic acid, and ethyl acetate.

The equilibrium constants for esterification reactions have been measured perhaps more frequently than is the case for any other type of reaction in liquid systems (excluding ionic equilibria), and the literature contains values for the equilibrium constants for the reactions between nearly all of the common

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[1] Recalculated by van't Hoff, *Ber.*, **10**, 669 (1877).

[2] Used in obtaining the value for K.

[3] Miss Tobin, Dissertation, Bryn Mawr College (1917).

acids and alcohols.[1] One or two cases are of special interest in illustrating the application of the mass law.

It has been shown by Menschutkin that esters of tertiary alcohols decompose usually into acid and unsaturated hydrocarbon, and the equilibrium conditions for such reactions have been studied by Konowalow,[2] and by Nernst and Hohmann.[3] The latter authors measured the equilibrium of the reaction between amylene and the chlorinated acetic acids, their results on trichloracetic acid at 100° C. being characteristic. The reaction proceeds according to the equation

$$CCl_3COOH + C_5H_{10} = CCl_3\,COOC_5H_{11}, \tag{167}$$

and we may write for it the mass law expression:

$$K_X = \frac{X \text{ ester}}{X \text{ acid} \times X \text{ amylene}}. \tag{168}$$

If 1.0 mol. of acid is mixed with a mols. of amylene, and if x represents the mols. of ester formed when the reaction has reached equilibrium, we may write equation (168) as

$$K_x = \frac{x \times N}{(a - x)(1 - x)}, \tag{169}$$

where N represents the total number of mols. Table VI contains a comparison of the values for x found experimentally for several values of a, and also those calculated from the mean value of the equilibrium constant.

TABLE VI

EQUILIBRIUM DATA

$(CCl_3COOH + C_5H_{10} = CCl_3COOC_5H_{11})$

Mols. C_5H_{10} a	Mols. CCl_3COOH	Mols. Ester x (Found)	Mols. Ester x (Calculated)
2.15	1.0	0.762	0.762
4.12	1.0	0.814	0.821
4.48	1.0	0.820	0.826
6.63	1.0	0.838	0.844
6.80	1.0	0.839	0.845
7.13	1.0	0.855	0.846

It is clear that there is very fair agreement between the observed and calculated values.

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[1] Menschutkin, *Ann. Chim. Phys.*, [5] **20**, 227 (1880), **23**, 14 (1881); **30**, 81 (1883).

[2] *Z. physik. Chem.*, **1**, 63 (1887); **2**, 6, 380 (1888).

[3] *Z. physik. Chem.*, **11**, 352 (1893).

A comparison of these data with those on p. 334 for the reaction between acetic acid and ethyl alcohol brings out an interesting difference in behavior. In the latter case the mols. of ester present at equilibrium increase rapidly with increasing mols. of alcohol added, and approach unity as the number of mols. of alcohol becomes large. In the case of the reaction between amylene and acid, the number of mols. of ester changes very slowly with an increase in the number of mols. of amylene. The reason is clear from comparison of equations (116) and (169). In equation (169) an increase in a produces an increase in N, and therefore x is much less affected than in the case of equation (166). In fact it can be shown that a might be made to approach infinity without increasing the value of x to more than about 0.88, provided equation (169) is valid over the entire range of concentrations.

The Effect of the Solvent: Many reactions in liquid media are carried out in the presence of a large excess of some indifferent constituent called the solvent. The theoretical implications of the addition of indifferent substances to equilibria have already been discussed, but the case of the solvent deserves particular consideration, as many experimental data are available upon equilibria in reactions in different media.

If we consider equations (106) and (107) and neglect the total pressure, we have

$$K_x = \frac{N_C^c \times N_D^d \cdots}{N_A^a \times N_B^b \cdots} \times N^{(a+b-c-d)} \tag{170}$$

and

$$K_c = \frac{N_C^c \times N_D^d}{N_A^a \times N_B^b} \times V^{(a+b-c-d)}. \tag{171}$$

From these equations it is clear that so long as the activity is equal to or proportional to the mol. fraction or the molecular concentration, addition of a solvent (which affects N and V) will be entirely without effect upon any equilibrium in which $a + b = c + d$. Berthelot and Péan de St. Gilles found this to be the case for the reaction between acetic acid and alcohol, using acetone as a solvent. If $a + b$ is not equal to $c + d$, the equilibrium concentrations will vary with the amount of solvent in accordance with equations (170) and (171), the equilibrium constants being unaffected. However, it frequently happens that the solvent may exercise a very marked influence upon the activity of some one or more of the reacting species, so that the relation between the mol. fraction and the activity no longer exists, and equations (170) and (171) are not valid. If the influence is sufficiently definite, we may, however, substitute another equilibrium equation. Thus, some reacting species may exist in a different molecular state in different solvents. Let us consider the general reaction

$$aA + bB = cC + dD, \tag{172}$$

for which in the absence of a solvent or in the presence of a really indifferent solvent we may write

$$K_x = \frac{X_C{}^c \times X_D{}^d}{X_A{}^a \times X_B{}^b}. \tag{173}$$

Let us consider this reaction carried out in a solvent in which the substance A exists almost entirely in the form of double molecules. For the equilibrium between single and double molecules we have the relation

$$K = \frac{X_A{}^2}{X_{(A_2)}}. \tag{174}$$

Now if X_A is very small as compared with $X_{(A_2)}$, that is, if nearly all of A is in the form of (A_2), we may write

$$X_A = K'\left(\frac{0.5X_A}{X}\right)^{1/2}, \tag{175}$$

where X_A represents the total number of mols. of A, calculated without regard to the molecular condition of A. If we substitute the value of X_A in equation (173), we obtain

$$K_x' = \frac{X_C{}^c \times X_D{}^d \cdots}{X_{(A_2)}{}^{a/2} \times X_B{}^b \cdots}, \tag{176}$$

where $X_{(A_2)}$ has the value of $\frac{0.5X_A}{X}$. We might have obtained this same equation by neglecting the single molecules of A entirely, and writing the reaction

$$\tfrac{1}{2}a(A_2) + bB \cdots = cC + dD \cdots, \tag{177}$$

for which the mass law equation would be

$$K_x = \frac{X_C{}^c \times X_D{}^d \cdots}{X_{(A_2)}{}^{a/2} \times X_B{}^b}. \tag{178}$$

Equations (176) and (178) are evidently identical

An example of a case of this type is given by the experiments of Nernst and Hohmann (*loc. cit.*) upon the esterification of amylene dissolved in benzene. The normal reaction of amylene and trichloracetic acid in the absence of a solvent proceeds according to equation (167), and the equilibrium relations are expressed by equations (168) and (169). In benzene solution, the acid exists almost entirely as double molecules, while the other substances behave normally.

If we mix together a mols. of amylene with 1.0 mol. of trichloracetic acid, and bring the mixture to equilibrium in benzene solution, we find the equilibrium no longer expressed by equation (169), but by the equation

$$K_x' = \frac{xX^{1/2}}{(a - x)(1 - x)^{1/2}}, \tag{179}$$

where K_x' has evidently a different numerical value from that of K_x in equation (169).

The actual equilibrium condition for a given reaction may obviously vary greatly with the nature of the solvent in which the reaction takes place, particularly if a marked difference exists in the molecular condition of the reacting species in the two solvents.

A very similar relation holds for reactions which may occur in the gaseous phase as well as in the liquid phase. Thus it has been shown that the equilibrium constant for the reaction between acetic acid and alcohol is very different in numerical value for the gaseous reaction from the value obtained for the reaction in the liquid phase.[1]

MATHEMATICAL TREATMENT OF EQUILIBRIUM DATA

When the equilibrium constant for a reaction has been determined, the calculation of the extent to which the reaction may proceed at that temperature, for different mixtures of the reacting constituents, is, in general, obvious. Examples have been touched upon in the preceding sections. The use of equations (70) and (79) and of the empirical equations representing the equilibrium constant as a function of temperature also necessitates no particular emphasis. The *indirect* calculation of equilibrium conditions, from consideration of the free energy decrease involved in the formation of chemical compounds, has such important possibilities that some further discussion seems justified.

The free energy increase accompanying a chemical reaction is ordinarily measurable by one of three methods, as indicated previously in an earlier section. It is related to the equilibrium constant by the equation

$$\Delta F = -RT \ln K_a. \tag{180}$$

It is related to the electromotive force of a reversible cell, in which the chemical reaction in question occurs through the operation of the cell, by the equation

$$\Delta F = -\mathbf{NFE} \tag{181}$$

(**N** is the number of faradays (**F**), equivalent to the reaction; **E**, the electromotive force).

It is related to the heat of reaction and the entropy change by the equation

$$\Delta F - \Delta H = -T\Delta S, \tag{182}$$

where ΔS is the increase in entropy.

Now the increase in free energy is a quantity determined by the initial and final states of the system, and therefore, when we write an equation expressing some definite change of state, the free energy increase accompanying the change is thereby fixed, whether or not it may be experimentally possible to carry out the reaction in question experimentally. Just as in thermochemistry we can combine equations for the calculation of the heat of reactions, so we may combine equations for the calculation of free energy increase, and, from it, equilibrium data. For a complete study of this subject, reference should be made to Lewis and Randall's Thermodynamics and Chemistry, which contains a systematic tabulation of free energy data, but certain examples will be given from their calculations to illustrate the method employed. It is, of course, immaterial whether the reactions in question are homogeneous or heterogeneous.

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[1] Edgar and Schuyler, *J. Am. Chem. Soc.*, 46, 64 (1924).

The reaction

$$H_2 + \tfrac{1}{2}O_2 = H_2O$$

must be written to correspond to some definite change of state in order to fix the free energy increase. Since the temperature of 25° C. is one at which many experimental data are available, and since atmospheric pressure is the usual experimental condition, we may write the reaction

$$H_2 \text{ (1 atm.)} + \tfrac{1}{2}O_2 \text{ (1 atm.)} = H_2O \text{ (gas, 1 atm.)}. \qquad (183)$$

Let us consider the calculation of the free energy increase of the reaction at 25° C.

(*a*) Direct determinations of the equilibrium constant for the reaction have been made at high temperatures, as pointed out in a previous section. From the mean results of these data, and from the heat of reaction and the heat capacities of the reacting constituents, it is possible to calculate, through equation (80), the free energy change at 25° C., although the extrapolation is over a very wide temperature range, which will magnify the error in any of the quantities involved. The result of such a calculation gives

$$\Delta F_{25^\circ \text{C.}} = -51{,}590 \text{ cal.}$$

(*b*) We may write the following series of equations, which added together give reaction (183):

$$\begin{array}{lrcl}
(1) & 2Ag + \tfrac{1}{2}O_2 & = & Ag_2O, \\
(2) & Ag_2O + H_2O_{(l)} & = & 2Ag^+ + 2OH^-, \\
(3) & 2Ag^+ + 2(e) & = & 2Ag, \\
(4) & H_2 & = & 2H^+ + 2(e), \\
(5) & 2H^+ + 2OH^- & = & 2H_2O_{(l)}, \\
(6) & H_2O_{(l)} & = & H_2O_{(gas)}.
\end{array}$$

The free energy change for the first reaction has been determined by direct measurement of the equilibrium, over the temperature range of 300° C. to 500° C. From the equilibrium constant it is possible to determine the free energy increase, and through equation (80), the value at 25° C. may be calculated. The value thus obtained is $\Delta F = -2395$ cal.

The free energy increase at 25° C. of reaction 2 is calculable directly through the equilibrium constant, for the solubility of Ag_2O has been measured at this temperature. The value thus obtained is $\Delta F = 21{,}040$ cal.

The sum of the free energy increases (3) and (4) may be obtained at 25° C. from measurements of the electromotive force of the cell, $Ag/AgCl/HCl/H_2$, and is $\Delta F = -36{,}896$ cal.

The free energy increase of reaction (5) is calculable in a number of ways, for example, from the ionization constant of liquid water, as determined from conductivity measurements, or from the electromotive force of "acid-alkali" cells. The best data give $\Delta F_{25° \text{C.}} = -38{,}210$ cal.

The free energy increase for reaction (6) is given from the equilibrium constant (vapor pressure) for the vaporization of water. At 25° C. we have $\Delta F = 2053$ cal.

Combining reactions 1–6, we have for reaction 183, $\Delta F_{25° \text{C}} = -2395 + 21{,}040 - 36{,}896 - 38{,}210 + 2053 = -54{,}408$ cal.

(*c*) Equation (183) may also be obtained by combining the following reactions:

$$
\begin{aligned}
&(1) \quad Hg(1) + \tfrac{1}{2}O_2 = HgO,\\
&(2) \quad H_2 + HgO = Hg(1) + H_2O(1),\\
&(3) \quad H_2O(1) = H_2O_{(\text{gas})}.
\end{aligned}
$$

The equilibrium constant for the first reaction has been determined by direct measurement, at the boiling point of mercury, and, by extrapolation through equation (80), we obtain at 25°, $\Delta F = -13{,}786$ cal.

From measurements of the electromotive force of the cell,

$$Hg/HgO_{(s)}/KOH_{(aq)}/H_2,$$

the free energy increase at 25° C. of reaction (2) may be calculated to be $\Delta F = -42{,}752$.

Combining these values with that of (3) determined above, we have for reaction (183), $\Delta F_{25° \text{C}} = -13{,}786 - 42{,}752 + 2052 = -54{,}485$ cal.

(*d*) Equation (183) may also be obtained by combining

$$
\begin{aligned}
&(1) \quad H_2 + Cl_2 = 2HCl_{(aq)},\\
&(2) \quad 2HCl_{(g)} + \tfrac{1}{2}O_2 = H_2O_{(\text{gas})} + Cl_2,\\
&(3) \quad 2HCl_{(aq)} = 2HCl_{(g)}.
\end{aligned}
$$

The free energy increase for reaction (1) may be calculated from measurement of the electromotive force of various cells, and is $\Delta F_{25° \text{C}} = -62{,}734$ cal.

The free energy increase for reaction (2) may be calculated from direct measurements of the equilibrium constant for the reaction, which by extrapolation to 25° C. give $\Delta F_{25° \text{C}} = -9120$ cal.

The free energy increase for reaction (3) may be obtained from equilibrium (vapor pressure) measurements of hydrochloric acid solutions:

$$\Delta F_{25° \text{C.}} = +17{,}350 \text{ cal.}$$

Combining these data, we obtain for reaction (183),

$$\Delta F_{25° \text{C.}} = -62{,}734 - 9120 + 17{,}350 = -54{,}504 \text{ cal.}$$

Finally, it is possible, through the third law of thermodynamics (see Chapter XVII), to calculate the free energy increase for reaction (183) from the entropies of hydrogen, oxygen and water, employing equation (182). The entropy change for the reaction, ΔS, is equal to $S_{H_2O} - S_{H_2} - \tfrac{1}{2}S_{O_2}$. The entropies of hydrogen and oxygen are known with a fair degree of certainty from measurements of the heat capacities of these substances at very low temperatures, and from theoretical considerations. The entropy of liquid water, from heat capacity data alone, is known only approximately,[1] but it may serve for a rough calculation, merely to illustrate the method of calculation. The best values, at 25° C., are

$$S_{H_2} = 29.44 \text{ cal./degree,}$$
$$\tfrac{1}{2}S_{O_2} = 24.0 \quad \text{''} \quad ,$$
$$S_{H_2O(l)} = 16.8 \quad \text{''} \quad .$$

ΔS, therefore, for the formation of liquid water at 25° C $= + 16.8 - 29.44 - 24.0 = - 36.64$ cal./degree.

For the heat of reaction at 25° C., $\Delta H = - 68{,}270$ cal., whence, by equation (182),

$$\Delta F - \Delta H = - T\Delta S,$$
$$\Delta F_{25^\circ \text{C}} = - 57{,}391 \text{ cal.}$$

Combining this value with the free energy of vaporization ($\Delta F = 2035$), we obtain for equation (183), $\Delta F = - 55{,}318$ cal.

It has thus been possible to calculate the free energy change for the formation of one mol. of gaseous water from its elements at 25° C. and atmospheric pressure by five methods, involving a wide range of experimental method and data from a variety of sources. The results may be repeated as follows:

$$(a) \quad \Delta F = - 54{,}590 \text{ cal.,}$$
$$(b) \quad \Delta F = - 54{,}108 \quad \text{``} \quad ,$$
$$(c) \quad \Delta F = - 54{,}485 \quad \text{``} \quad ,$$
$$(d) \quad \Delta F = - 54{,}504 \quad \text{``} \quad ,$$
$$(e) \quad \Delta F = - 55{,}318 \quad \text{``} \quad .$$

If the mean of these values, or preferably the most probable value based upon the certainty with which the particular experimental data are known, be taken, and combined with the values for the heat of the reaction and the heat capacities of hydrogen, oxygen and water, we may by equation (80) express ΔF as a function of temperature (see Chapter II) which will permit the calculation of the equilibrium constant and hence the equilibrium concentrations for any desired conditions of temperature, pressure, or proportions or reactants.

This reaction has been discussed at length because it illustrates extremely well the value of an exact knowledge of the free energy change in reactions, and the methods by which equilibrium calculations may be made through a study of these free energy increases. If the free energy increase of formation of all chemical compounds were available, it would be possible, theoretically, to calculate the equilibrium constants for any reaction which one might choose to write, whether or not such reaction were experimentally feasible. It is all too frequently true that experimental data are unavailable or uncertain in particular cases. This only emphasizes the need for systematic investigations in this direction, and for an exact understanding of the factors involved in chemical equilibrium.

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[1] Lewis and Gibson, *J. Am. Chem. Soc.*, **39**, 2554 (1917).

CHAPTER IX

HETEROGENEOUS EQUILIBRIUM

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Any system composed of two or more phases may be the seat of heterogeneous equilibria as well as of homogeneous equilibria. Where the chemical or physical reactions which have reached a condition of equilibrium are wholly confined to a single phase, the equilibrium is regarded as homogeneous; such would be the equilibrium between the dissolved molecules of sodium chloride and the ions which they form. When however the reactions which occur involve a movement of molecules from one phase to another, the equilibrium attained is spoken of as heterogeneous; such equilibria exist for example in the evaporation and condensation of water, or in the dissolving and precipitation of a solid salt in water.

It is quite obvious that heterogeneous equilibria can not be more simple than those occurring in homogeneous systems; indeed, they may frequently be much more complex. In many cases the equilibria are greatly affected by the surface conditions at the interface between the phases; such cases are dealt with in the chapter on colloid chemistry. In the present chapter the discussion will be restricted to those cases of heterogeneous equilibria in which only temperature, pressure and concentration are effectual influences. For these cases there are known two fundamental principles which are sufficient for systematizing practically all the phenomena; these principles are known as the Distribution Law and the Phase Rule. The former of these, which will be studied first, is quantitative in nature and, within certain limits, is of very great value in defining heterogeneous equilibria; the latter and broader principle will be studied at a later point in the chapter.

THE DISTRIBUTION LAW

The distribution law expresses a mathematically constant ratio between the concentrations of a given molecular species in any two phases of a system at constant temperature. It expresses the ratio equally well whatever possible combination of gaseous, liquid or solid phases is under observation. It has however required a long period of time for this entirely general form of the law to be recognized; initially only special combinations of phases were known to fall within its scope. The first statement of the law, covering only the equilibrium between a gas and its solution in a liquid, was made by William

Henry,[1] and is commonly referred to as Henry's law. At a later date, Berthelot and Jungfleisch [2] studied the partition of iodine between carbon disulphide and water, and stated the applicability of the principle to the distribution of a dissolved body between two liquid phases. Nernst,[3] studying distribution in systems of the same type (liquid-liquid), added the important restriction that a constancy in the distribution ratio can exist only between those molecules of the distributed substance which are in the same condition in both phases, pointing out that no immediate equilibrium and hence no immediate distribution can occur between simple molecules in one phase and associated molecules in a second phase, or between simple molecules and their dissociation products in different phases.

DISTRIBUTION IN THE SYSTEM GAS-LIQUID

The equilibrium existing between a gas and its solution in a liquid is found to follow the law of Henry, who was the first to observe the simple relationship which exists. Henry's law may be stated as follows: the mass of a gas absorbed or dissolved by a given volume of a liquid is proportional to the pressure of the gas, at constant temperature. A simple algebraic statement of the law takes the form

$$\frac{m}{p} = K_1,$$

where m is the mass absorbed and p the pressure of the gas. This equation is easily changed so as to show the volume of the gas absorbed instead of its mass. The mass is proportional to the volume, by Avogadro's hypothesis, and is likewise proportional to the pressure, by Boyle's law; i.e., $m = pvK'$. If this value be substituted for m in the first equation, it becomes

$$v = \frac{K_1}{K'} = K_2;$$

that is, the volume of gas absorbed is independent of the pressure. Still a third form may be derived from the first; if mass m of the gas be absorbed in unit volume of the liquid, the amount present constitutes the concentration in the liquid phase and may be written C_2; in the gaseous phase the concentration C_1 is proportional to the pressure; introducing these values for m and p in the equation and inverting,

$$\frac{C_1}{C_2} = K_3.$$

This is the most generalized expression for Henry's law, and is likewise a direct algebraic statement of the distribution law, namely, that *the concentrations of*

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[1] *Phil. Trans.* (1803); *Gilbert's Annalen*, **20**, 147 (1805).

[2] Berthelot and Jungfleisch, *Ann. chim. phys.*, (4) **26**, 396 (1872).

[3] Nernst, *Z. physik. Chem.*, **8**, 110 (1891).

any single molecular species in two phases at equilibrium bear a constant ratio to each other, **the temperature remaining constant.**

Henry's law may be predicted qualitatively from the theorem of Le Chatelier, which is of the broadest applicability. According to this theorem a system at equilibrium, if subjected to a stress, will undergo a change of equilibrium tending to reduce the intensity of the stress. Obviously the pressure exerted upon a gas will be reduced by any change which reduces the volume. Since the solution of a gas always produces a reduction in the total volume of a system, it follows that an increased solubility of gas will result from an increase of pressure, which is a qualitative statement of Henry's law.

One of the early applications of Henry's law was made by Dalton [1] in the experimentation on which his well-known law of partial pressures is based. Dalton deduced from his experiments that in a mixture of gases the absorption of each by a liquid is proportional to its own pressure, and not to the total pressure It is thus shown that Henry's law applies to each component of a mixture of gases as well as to a single gas.

The experiments of Bunsen [2] subjected the law of Henry to a fairly rigorous test. Bunsen determined the weight of carbon dioxide gas dissolved by a fixed quantity of water at a number of pressures, all less than one atmosphere. In Table I, which includes some of Bunsen's results, the column headed P gives the experimental pressures in meters of mercury and g the weight of gas dissolved by a fixed volume of water.

TABLE I

SOLUBILITY OF CO_2 IN WATER

Temperature	No.	P	g	P/P_1	g/g_1
19.9° C.	1	0.7255	38.61	—	—
"	2	0.5245	27.24	1.38	1.42
"	3	0.5237	27.08	1.39	1.43
"	4	0.5231	27.28	1.39	1.42
3.2°	1	0.5244	31.41	—	—
"	2	0.6467	38.66	0.8109	0.8125
"	3	0.6470	38.49	0.8109	0.8161

Taking the results at a fixed temperature, as at 19.9° C., the pressures of experiments 2, 3 and 4 are compared with those of experiment 1, giving the ratio P/P_1, and in like manner the ratio g/g_1 is that of the weights absorbed. Strict compliance with Henry's law would require that the ratios have the same value, the agreement is not perfect, but within the probable experimental error. Further experiments by Bunsen, by Khanikow and Luganin,[3] and by others,[4] together with the early work of Henry and of Dalton, have established that, for moderate pressures, the law of Henry holds with at most small variation.

Notwithstanding this satisfactory condition, there have been numerous cases where experimental results and the requirements of Henry's law diverge greatly. These deviations fall into two principal classes. Many of the apparent discrepancies are due to the application of the law without reference to the important restrictions pointed out by Nernst (*loc. cit.*), and can be brought into harmony by comparatively simple mathematical correction;

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[1] *Memoirs Literary and Phil. Soc. of Manchester*, **1**, 1805, *Gilbert's Annalen*, **28**, 397 (1808).

[2] Bunsen, *Ann.*, **93**, 1 (1855).

[3] *Ann. chim. phys.*, (4) **11**, 412 (1867).

[4] Ostwald, *Lehrbuch*, **I**, 620 (Leipzig, 1903).

other cases appear to be due to the condition of high concentration and indicate that Henry's law, like other gas laws, is strictly applicable only to ideally dilute gases and fails to represent the facts when the concentrations become large. Each of these types of deviation is worth careful study.

The fact that the unmodified law of Henry could not properly be applied to cases where chemical action occurs between the gas and liquid was recognized by Bunsen (*loc. cit.*) and was doubtless in the mind of all careful workers in the field. It remained for Nernst (*loc. cit.*) to state in more precise terms what was hinted at in the vaguely used phrase, chemical action; and although Nernst's argument was developed for systems of two liquids, it applies just as logically where the gaseous phase is concerned. Nernst shows that we cannot logically think of a substance as distributed between two phases if its molecular condition in the two phases is different; for example, double molecules, formed by association in one phase, cannot be in immediate equilibrium with unassociated molecules in a second phase. If however the associated molecules in the first phase undergo reversible dissociation so that an equilibrium between associated and unassociated molecules exists in that phase, then an equilibrium will exist between the unassociated molecules in the two phases. The constant ratio of concentrations should be found, therefore, not between the total concentrations in the two phases, but between the concentrations of that molecular species which is common to both phases. Such an equilibrium can be illustrated by the following scheme, in which xy represents the simple molecules and $(xy)_n$ the associated molecules:

$$\begin{array}{rl} \text{gaseous phase:} & xy \\ & \downarrow\uparrow \\ \text{liquid phase:} & n\cdot xy \rightleftharpoons (xy)_n. \end{array}$$

If the substance in the liquid phase undergoes direct combination with the solvent, which will be represented by S, the diagram becomes

$$\begin{array}{rl} \text{gaseous phase:} & xy \\ & \downarrow\uparrow \\ \text{liquid phase:} & xy + nS \rightleftharpoons xy\cdot nS. \end{array}$$

A further possibility is that of dissociation, either electrolytic or non-electrolytic:

$$\begin{array}{rl} \text{gaseous phase:} & xy \\ & \downarrow\uparrow \\ \text{liquid phase:} & xy \rightleftharpoons \overset{+}{x} + \overset{-}{y}. \end{array}$$

In addition to these three possibilities, cases will frequently occur in which any two or even three of these equilibria are met in the liquid phase. It is clear that if Henry's law is to be evaluated for any such instances, the constants for these homogeneous equilibria must be known, so that the true concentration of the distributed substance in each phase may be calculated from the total concentration present.

The case in which combination occurs between the distributed substance and the solvent, as indicated in the second scheme above, is actually freer from complications than might appear. In such an instance, Henry's law is applied to the distribution equilibrium and the mass law is applied to the reaction occurring in the liquid phase between the distributed molecules and the solvent. If now

C_1 = concentration of distributed molecules in the gaseous phase,
C_2 = concentration of distributed molecules in the liquid phase,
C_s = concentration of solvent molecules,
C_c = concentration of compound molecules,

the two laws may be written as follows:

$$\frac{C_1}{C_2} = K \text{ (Henry's law);} \tag{1}$$

$$\frac{C_2 \times (C_s)^n}{C_c} = K_1 \text{ (law of mass action).} \tag{2}$$

The concentration of solvent molecules C_s is very large and does not vary appreciably in dilute solution; $(C_s)^n$ may therefore be written as a constant and the law of mass action becomes

$$\frac{C_2}{C_c} = K_2. \tag{3}$$

Combining equations (1) and (3), the complete equation becomes

$$\frac{C_1}{C_2 + C_c} = K_3.^1 \tag{4}$$

It is thus shown that Henry's law may be tested according to equation (4), in which the sum $C_2 + C_c$ is the *total* concentration of the gas in the liquid phase as it would be ordinarily determined by analysis. The occurrence of compound formation therefore will have no influence upon Henry's law except to change the numerical value of the constant.

The case is quite different however if association or dissociation occur; it then becomes necessary to take the extent of these changes into account.

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[1] The algebraic derivation is as follows: by inversion of equation (3),

$$\frac{C_c}{C_2} = \frac{1}{K_2},$$

whence

$$\frac{C_c + C_2}{C_2} = \frac{1 + K_2}{K_2}$$

divided into equation (1),

$$\frac{C_1}{C_2 + C_c} = \frac{KK_2}{1 + K_2} = K_3.$$

The algebraical treatment again is based upon the use of the mass law to express the degree of dissociation or association. Let C now stand for the total concentration in the liquid phase as analytically determined, and α stand for the degree of dissociation; then the mass law expression will be, for a binary electrolyte,

$$\frac{(C\alpha)^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} = K_m,$$

whence

$$\alpha = \frac{-K_m + \sqrt{K_m^2 + 4K_mC}}{2C}.$$

Writing Henry's law in the same terms as before, and remembering that C_2, the concentration of undissociated molecules in the liquid phase, is equal to the fraction $(1 - \alpha)$ of the total concentration C,

$$K = \frac{C_1}{C_2} = \frac{C_1}{C(1-\alpha)} = \frac{2C_1}{2C + K_m - \sqrt{K_m^2 + 4K_mC}}.$$

Henry's law may therefore be tested for a compound which undergoes dissociation (electrolytic or non-electrolytic) by analysis of the gaseous and liquid phase, if the dissociation constant K_m is also known and the total concentrations in the two phases, C and C_1, be determined.

The solubility of ammonia in water may be studied according to this method. The equilibria here are as follows:

$$\begin{array}{ll} \text{gaseous phase:} & NH_3 \\ & \downarrow\uparrow \\ \text{liquid phase:} & NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows \overset{+}{NH_4} + \overset{-}{OH}. \end{array}$$

Here the formation of the compound NH_4OH is without effect on the form of the equations, as shown above, and the dissociation constant is known. Calingaert and Huggins[1] have tested dilute solutions of ammonia from a concentration of 1.25 gms. to .005 gm. per liter at 100°. The column headed C in Table II gives the total concentration in the liquid phase, in gms. per liter of solution, the column C_1/C the experimentally found ratio in the two phases, $1 - \alpha$ the undissociated fraction of the ammonium hydroxide in the liquid phase, and k the constant for Henry's law, obtained by the equation $k = C_1/C(1 - \alpha)$.

TABLE II

AMMONIA AND WATER AT 100°

C	$K = \frac{C_1}{C}$	$1 - \alpha$	$k = \frac{C_1}{C(1-\alpha)}$
1.256	12.92	0.987	13.1
0.633	12.67	0.981	12.9
0.305	12.44	0.973	12.8
0.148	12.13	0.963	12.6
0.0386	12.06	0.926	13.0
0.0190	11.83	0.896	13.2
0.0107	11.53	0.864	13.3
0.0046	11.05	0.806	13.6

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[1] *J. Am. Chem. Soc.*, **45**, 915 (1923).

It is apparent that, when the dissociation is ignored, as in column 2, the quotient shows a regularly diminishing value, but, when the correction for dissociation is introduced, as in column 4, there is a satisfactory constancy. The solutions are all, it will be noted, very dilute, and the gas pressure correspondingly low.

When the gas pressures used are large, deviations from Henry's law are found which cannot be compensated for by assuming polymerization or dissociation. Deviations of this sort were noted by Roscoe and Ditmar [1] and by Sims.[2] When the pressures are no larger than one or two atmospheres, variations of considerable magnitude appear. The variation was found to be dependent also on the temperature; thus, at 0°, the solubility of ammonia in water fails to follow the law, while at higher temperatures a much closer approximation to the law is obtained. Although the correction for electrolytic dissociation of the ammonia has not been applied here, such a correction would have no important effect, as the dissociation is extremely small at these concentrations. The results are shown graphically in Fig. 1. The straight line in each case gives the ideal curve; its slope is fixed by the position of the point *b*, which is taken from the observed data at 76 cm. pressure. At 0°, the curve for the absorption of ammonia shows that the absorption is greater than calculated by the law when the pressures are low, but is less than the requirement at higher pressures. The isothermal curves at 20°, 40° and 100° indicate that as the temperature rises the absorption approaches more nearly the theoretical, the pressures still being low.

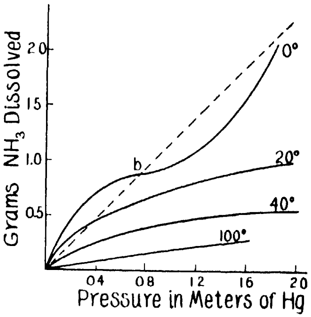

FIG. 1. Solubility of Ammonia at Varying Temperatures and Pressures

Extensive experimentation by Sander [3] has shown still greater deviations from the law when the pressures are high. The absorption of carbon dioxide in water, alcohols, ether, aromatic hydrocarbons and other organic solvents led to the following conclusions. The solubility of carbon dioxide at pressures of 20 to 140 kg. per square centimeter varies from Henry's law at low temperatures, but approaches the required values at higher temperatures, at 100° the solubility is proportional to the pressure within the experimental error. With respect to the extent of deviation at low temperatures, it is less in water, and greater in all the organic solvents; this comparison makes it clear that the deviations are not caused by electrolytic dissociation whether or not association plays a part. As a correction of interest, it is found that a closer approximation to Henry's law is found if the weight of absorbed gas is referred to the volume of the solution rather than to that of the pure solvent.

The above variations observed by Sander occur when the concentration in the gaseous phase is very high, under which condition the general equation of state for a gas, $PV = RT$, is likewise known to fail. The question arises whether high concentrations in the liquid

[1] Roscoe and Ditmar, *Ann.*, **112**, 349 (1859).

[2] *Ann.*, **118**, 345 (1861).

[3] Sander, *Z. physik. Chem.*, **78**, 513 (1912).

phase bring about a similar result. The experiments of Sackur[1] appear to answer that question in the negative, at least for the gas carbon dioxide in several organic liquids. Sackur selected methyl alcohol, ethyl alcohol, acetone, methyl acetate and ethyl acetate for solvents at very low temperatures, under which conditions the solubility is very high while the vapor pressure of the gas is low. The results of his experiments are given in part in Table III. The figures under P represent the pressure of the gaseous phase in mm. of mercury, those under K the constant for Henry's law, but with the terms in such order that the ratio is that of the concentration in the liquid phase to that in the gaseous phase.

TABLE III

Solubility of Carbon Dioxide in Methyl Alcohol

P	K at $-78°$	K at $-59°$
50	120.5	—
100	119.6	42.5
200	120.1	42.7
400	122.2	43.1
700	126.8	—
740	—	43.3

The values of the constant show but slight variation through a considerable range, indicating that up to high concentrations in the liquid phase there is little modification of the law necessary; the variation in the case of the other solvents is slightly greater. When the constant is calculated on the basis of mass of gas absorbed per unit volume of solvent instead of solution, the variation is much greater, which result is in accord with that already noted by Sander (*loc. cit.*).

The solubility of hydrogen chloride in water is an interesting case of an exception to Henry's law. Roscoe and Ditmar (*loc. cit.*) have investigated the dependence of this solubility upon the pressure. Since the compound is a strong electrolyte, it is apparent that a correction of very large magnitude must be made if the law is to have a proper test, and this has not yet been done. It appears from the experiments however that the gas has a very considerable solubility in water even when the pressure has become too low to be measurable. Ostwald[2] interprets this result, through graphic extrapolation of the solubility curve, to mean that there is a residual solubility which is independent of the pressure, but varying in composition with the temperature. This is in agreement with the experiments of Richards and Singer,[3] who found that a tenth-normal solution of hydrochloric acid emits only a negligible amount of acid upon prolonged boiling.

A survey of these and similar investigations leads to the general conclusion that Henry's law, like other gas laws, is strictly applicable only to ideal gases, and fails to express exact relations as the gas departs from ideal conditions.

The foregoing discussion of Henry's law has been based upon the absorption of the gas at constant temperature. A question naturally arises as to the change in value of these absorption coefficients with change of temperature. But little of an entirely general character has been learned. There is, of course, no doubt that van't Hoff's law of mobile equilibrium applies here; if the temperature of a system at equilibrium is raised, that reaction occurs which is accompanied by the absorption of heat, i.e., the endothermal reaction. If it is known therefore that the process of solution of a gas, at the equilibrium concentration, is an endothermal change, it follows qualitatively that the solubility of that gas will increase with increasing temperature, and in cases where solution is exothermal the reverse will be true. It is an empirical fact that the dissolving of a gas is an exothermal process in the majority of cases, whence it follows that the solubility decreases with the temperature; in such cases, the constants of Henry's law will then show a decreasing value with increase of temperature, or, to phrase the same relation otherwise, the gas will have a negative solubility coefficient. But this is by no means always the case; the temperature coefficient is found to be positive in some instances, and in a few cases passes from a positive through a zero value to a negative value as the temperature changes. A few instances will show that all such are possible.

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[1] *Z. Elektrochem.*, **18**, 641 (1912).

[2] Ostwald, *Lehrbuch*, **I**, 623. Leipzig, 1903.

[3] *Am. Chem. J.*, **27**, 208 (1902).

Bunsen (*loc. cit.*) believed that hydrogen in water and also oxygen and carbon monoxide in alcohol all have a zero temperature coefficient; Winkler and Bohr[1] find however that hydrogen has a negative coefficient at low temperatures, passing through a zero value at about 60° and having a positive value above that temperature. Just[2] has made an extensive study of the solubility of nitrogen, hydrogen and carbon monoxide in water and in a large number of organic solvents, at 20° and 25°; the temperature coefficient is positive in all solvents except water. For carbon dioxide, on the other hand, Sander (*loc. cit.*) finds a negative coefficient in all solvents, with nitrobenzene as a possible exception. Geffken's[3] figures for the solubility of carbon dioxide in water may be regarded as a fairly typical case; the temperature coefficient is negative, as shown in Table IV, where the Bunsen absorption coefficient is indicated by the values of β at different temperatures; it is defined as the volume of gas, measured under standard conditions, absorbed by unit volume of solvent.

TABLE IV

SOLUBILITY OF CARBON DIOXIDE IN WATER

Temperature	β	Temperature	β
0	1.713	25	0.759
5	1.424	30	0.665
10	1.194	40	0.530
15	1.019	50	0.436
20	0.878	60	0.359

The distribution law can be applied to simpler systems of gases and liquids than those discussed above, namely, to systems consisting of a single liquid and its vapor. At a constant temperature the ratio of concentrations in the two phases should be constant, which is equivalent to the statement that a pure liquid has a single fixed vapor pressure. If one considers the possibility of a pressure change, it appears that it has little effect upon the concentration of the liquid phase within reasonable limits, since the compressibility of liquids is of exceedingly small magnitude; the concentration in the liquid phase being therefore practically constant, the distribution law indicates that the concentration in the gaseous phase will likewise remain substantially unchanged. If a higher total pressure is put upon the system through the agency of some second gas which is introduced, the pressure of the distributed phase (i.e., the vapor of the liquid) will vary but slightly. The *exact* relationship which exists between the vapor pressure exerted by a liquid and the applied external pressure has already been given in Chapter IV, page 120.

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[1] *Wied. Ann.*, **62**, 644 (1897).

[2] *Z. physik. Chem.*, **37**, 342 (1901).

[3] *Z. physik. Chem.*, **49**, 271 (1904).

Not only may the vapor tension of a pure liquid be shown to be a constant by application of the distribution law, but it is also possible by the same means to arrive at a derivation of Raoult's law, which expresses the depression of vapor pressure of a solvent upon addition of a solute. Let N equal the number of mols. of pure solvent taken for consideration, to which n mols. of solute are added; the molar concentration of solvent then falls from N/N to $N/(N+n)$. The distribution law requires however that the ratio of concentrations of the solvent in the gaseous and liquid phases remain constant; whence, writing C_0 and C as the concentrations of solvents in the two gaseous phases,

$$\frac{C_0}{N/N} = \frac{C}{N/(N+n)},$$

$$\frac{C_0}{C} = \frac{N+n}{N},$$

$$\frac{C_0 - C}{C_0} = \frac{n}{N+n}.$$

Since the pressures in the gaseous phases are proportional to the concentrations, and representing these pressures by p_0 and p,

$$\frac{p_0 - p}{p_0} = \frac{n}{N+n},$$

which is the familiar form of Raoult's law for ideal solutions.[1]

DISTRIBUTION IN THE SYSTEM LIQUID-LIQUID

The distribution law has had its principal test in the case of liquid-liquid systems; furthermore, the application of the law to such systems has yielded most interesting and useful results and made possible the interpretation of a large number of otherwise inexplicable facts. Berthelot and Jungfleisch (*loc. cit.*) were the first to make a systematic investigation of systems of this sort and to note the general underlying law. The following table (Table V) gives some of their experimental results.

Inspection of the values of K in these tables shows that constancy in an exact sense is not attained, which fact was not overlooked by the experimenters themselves; but the approximation to constancy in these cases, in which the actual concentrations are varied considerably, is sufficient to indicate the underlying principle. In the case of the two acids no consideration of dissociation was taken into account, as the work antedated the dissociation theory. Other cases of distribution between two liquids have been studied in large number,[2] and in the majority of cases considerations of dissociation or association are necessary before the constancy of ratio can be detected; but, it is also true that, in addition to the cases of iodine and bromine in carbon disulphide and water as tabulated by Berthelot and Jungfleisch, there is a considerable number of

[1] For a discussion of Raoult's law, see Kendall, *J. Am. Chem. Soc.*, **43**, 1391 (1921).

[2] See Herz, *Der Verteilungssatz*, Stuttgart, 1909.

TABLE V

DISTRIBUTION OF SOLUTE BETWEEN TWO LIQUIDS

Iodine in Carbon Disulfide and Water at 18°			Bromine in Carbon Disulfide and Water at 20°		
Gms. I per 10 cc. H_2O	Gms. I per 10 cc. CS_2	$K = \frac{C_1}{C_2}$	Gms. Br per 10 cc. H_2O	Gms. Br per 10 cc. CS_2	$K = \frac{C_1}{C_2}$
0.0041	1.74	420	0.176	10.2	58
0.0032	1.29	400	0.030	2.46	82
0.0016	0.66	410	0.020	1.55	78
0.0010	0.41	410	0.0011	0.09	80
0.00017	0.076	440			

Succinic Acid in Ether and Water at 15°			Oxalic Acid in Ether and Water at 11°		
Gms. Acid per 10 cc. H_2O	Gms. Acid per 10 cc. Ether	$K = \frac{C_1}{C_2}$	Gms. Acid per 10 cc. H_2O	Gms. Acid per 10 cc. Ether	$K = \frac{C_1}{C_2}$
0.486	0.073	6.6	0.473	0.052	9.0
0.420	0.067	6.3	0.436	0.046	9.5
0.365	0.061	6.0	0.304	0.031	9.8
0.236	0.041	5.7	0.203	0.0205	9.9
0.121	0.022	5.4			
0.070	0.013	5.2			
0.024	0.0046	5.2			

other instances in which the uncorrected ratio in two liquids, as determined by analysis, is reasonably constant over quite large variations in the actual concentrations. Such cases include hydrogen peroxide[1] in water and various organic liquids, boric[2] acid in water and amyl alcohol, bromine[3] in water and bromoform, iodine[3] in water and chloroform and in water and ethylene glycol, and phenol[4] in water and amyl alcohol.

If a true constancy in the value of *K* is assumed for a simple case of distribution between two liquids, as in the instances referred to, an interesting corollary follows. The addition of a larger total quantity of solute will not alter the ratio of concentrations in the two layers, and the process may be imagined as continued until one of the phases is saturated with respect to the solute. The question arises as to the effect of further addition of solute. It cannot enter the phase assumed to be saturated, by definition of the term; nor can it enter the other phase by the assumption of the distribution law, since its further solution would alter the value of the constant. It follows then that both phases are saturated with respect to the solid and that the distribution ratio is the ratio of the solubilities of the solute in the two solvents. From this process of reasoning it results that the distribution law is frequently so phrased as to state that the distribution ratio of a solute between two solvents is the ratio of its solubilities in the two solvents. This is of course an entirely logical statement on the assumption that no correction factors are necessary; but, as a matter of fact, no data have yet been assembled which support this simple statement, and it is probable that it is true only for the distribution of very insoluble substances; for, it will be shown that, in the case of liquid systems, as it has already been shown for the system gas-liquid, the distribution law is strictly applicable only to ideally dilute solutions.

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[1] Calvert, *Z. physik. Chem.*, **38**, 513 (1901), Walton and Lewis, *J. Am. Chem. Soc.*, **38**, 633 (1916).

[2] Abegg, Fox and Herz, *Z. anorg. Chem.*, **35**, 129 (1903).

[3] Jakowkin, *Z. physik. Chem*, **18**, 585 (1895).

[4] Herz and Fischer, *Ber.*, **37**, 4746 (1904); **38**, 1138 (1905); Landau, *Z. physik. Chem.*, **73**, 200 (1910).

If the distribution ratio is to be constant in systems consisting of two liquids, there is another assumption that must be made, namely, that the two liquids are mutually insoluble, or, at any rate, do not have their mutual solubility altered by the presence of the distributed substance. In actual experimentation this condition has not been and probably cannot ever be strictly realized; actually the distributed substance does have an effect upon the mutual solubility, and that effect may vary both in amount and in direction. The distributed phase may lower the mutual solubility; in such a case it is conceivable that the mutual solubility might be reduced to zero by successive additions of solute, so that the limiting distribution ratio would be that of the solubilities in the pure solvent. The solubility of one liquid in the second may increase and that of the second in the first decrease by the addition of solute; in this case it is clear that the distribution ratio must vary throughout the whole range of concentrations. The third possibility is that the mutual solubilities of the two solvents are increased by addition of the solute; this will bring about a most interesting condition which will be more fully discussed from the standpoint of the phase rule under three-component systems. The obvious result of adding more and more solute in such an instance is to make the two liquid phases more and more like each other in composition until they become identical and dissolve in each other in all proportions. At this consolute concentration the ratio of the distributed compound in the two phases must be unity, as was pointed out by Klobbie[1] in the case of malonic acid dissolved in water and ether. There will in such cases be a variation of the ratio from whatever value it has in dilute solution to unity at the consolute concentrations, provided only that the liquid phases continue to dissolve the solute up to this point of complete mutual solubility. Any one of these three possibilities discussed above may be realized experimentally, and it is apparent therefore that the assumption of complete insolubility of the two liquids is, in the nature of things, not realizable when a third substance is added. If, however, the concentrations of the third substance are kept sufficiently small, this effect may be of negligible dimensions; it appears therefore that, for liquid-liquid systems, as well as for gas-liquid systems, the distribution law may be applied successfully only when the solutions are dilute. It will be seen in the examples given that this requirement has been kept in mind when success has been attained.

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[1] *Z. physik. Chem.*, **24**, 629 (1907).

Correction for Dissociation and Association. It has already been pointed out, in the discussion of Henry's law, that corrections for dissociation and association are necessary where these phenomena occur; the additional complication in liquid-liquid systems is that these corrections may be found necessary for both phases. Nernst (*loc. cit.*) modified the distribution law so as to make it applicable to such systems, stating the conditions as follows:

1. If the dissolved substance has the same molecular weight in both solvents, it possesses a distribution coefficient independent of the concentration, and vice versa.
2. If the dissolved substance consists of molecules of different weight or composition, the above first rule holds for each molecular species.

It has been pointed out in the discussion of Henry's law that, in the phase in which dissociation occurs, the total concentration, as determined analytically, is to be multiplied by the term $(1 - \alpha)$ before insertion in the distribution formula, where α is the fractional dissociation. It now remains to be shown how cases may be treated where the disturbing condition is that of association. Reference to Fig. 2 will indicate the proper method of reasoning. Let X represent the molecular species common to both liquid phases, and let it be associated in one phase to form double molecules, indicated as $(X)_2$. Analysis of the phase marked I gives us the concentration of X in that phase, represented by C; but analysis of phase II gives, not the concentration of X, which is necessary for testing the distribution law, but a concentration C_1 made up from both associated and non-associated molecules. The necessary term may be derived however by the application of the mass law to the equilibrium occurring in phase II. If α be the fractional dissociation into simple molecules, then

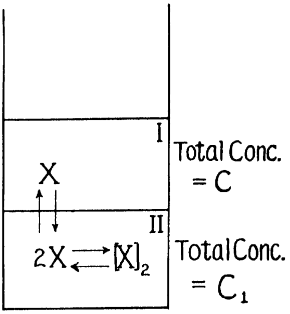

FIG. 2. Distribution Diagram for an Associated Compound

$$\frac{(C_1\alpha)^2}{C_1(1 - \alpha)} = K, \qquad C_1\alpha = \sqrt{C_1(1 - \alpha)K}.$$

Now $C_1\alpha$ is the concentration of simple molecules, and may be inserted in the distribution ratio:

$$K = \frac{C}{C_1\alpha} = \frac{C}{\sqrt{C_1(1 - \alpha)K}},$$

$$\frac{C}{\sqrt{C_1(1 - \alpha)}} = K'.$$

It will be seen that if the association were into molecules three times the weight of the simplest molecule, the radical would become a cube root, and, in more general terms, for association into a molecule $(X)_n$ the denominator would become an nth root. Considering however only the simpler cases of dissociation of a binary compound and association into double molecules, the following general formulæ have been developed:

$$\left.\begin{array}{l}\text{Phase I, neither association nor dissociation,}\\ \text{Phase II, neither association nor dissociation,}\end{array}\right\}\frac{C}{C_1}=K;$$

$$\left.\begin{array}{l}\text{Phase I, dissociation occurring,}\\ \text{Phase II, no molecular change occurring,}\end{array}\right\}\frac{C(1-\alpha)}{C_1}=K;$$

$$\left.\begin{array}{l}\text{Phase I, no molecular change occurring,}\\ \text{Phase II, association occurring,}\end{array}\right\}\frac{C}{\sqrt{C_1(1-\alpha)}}=K;$$

$$\left.\begin{array}{l}\text{Phase I, dissociation occurring,}\\ \text{Phase II, association occurring,}\end{array}\right\}\frac{C(1-\alpha)}{\sqrt{C_1(1-\alpha')}}=K.$$

In these general formulæ, C and C_1 represent the concentrations as analytically determined, α and α' the degree of dissociation as determined by independent methods; and the further assumptions are included that the degree of dissociation follows the mass law and that the distributed species is the simple molecule.

In several of the cases to be discussed, an algebraic simplification is possible for cases where association occurs. In benzene and similar hydrocarbons it happens that association is frequently complete or nearly so; the value of α therefore becomes very small as compared with unity in the term $(1 - \alpha)$, and may be neglected, so that the ratio becomes

$$C/\sqrt{C_1} = K,$$

thus rendering unnecessary any quantitative knowledge of the association equilibrium.

Nernst's generalizations, which are included in the foregoing discussion, receive support from his own experiments and more particularly from those of Hendrixson.[1] In Table VI are given the data for one of a series of eight careful distribution experiments in cases involving both dissociation and association. The predictions of the theory are fulfilled if it can be shown that, assuming a constant distribution ratio for the simple molecules of benzoic acid between water and benzene, the degree of molecular dissociation in the benzene phase follows the mass law. For this discussion, let

C_1 = the total concentration in the aqueous phase,
C_2 = the total concentration in the benzene phase,
α = the degree of electrolytic dissociation in the water,
k = the distribution ratio of simple molecules between water and benzene,
m_1 = the concentration of simple molecules in the benzene,
K = the molecular dissociation constant in the benzene.

The constancy of the values of K is to be proved, and it is obvious that it is some function of the distribution constant k. Of the terms listed above,

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[1] *Z. anorg. Chem.*, **13**, 73 (1897).

C_1 and C_2 are determined by analysis of the two phases at various total concentrations; α may be calculated from the Ostwald mass law for the dissociation of benzoic acid in water, $\frac{\alpha^2}{(1 - \alpha)V} = 0.00006$. The value of k, the distribution constant, is arrived at by the following reasoning; it is of course the ratio of the simple molecules in the two phases, whence $k = \frac{C_1(1 - \alpha)}{m_1}$. The equation, however, includes both k and m_1 as unknown terms. Proceeding further, K, the molecular dissociation constant in the benzene phase, has its value expressed by the application of the mass law to the equilibrium $2C_6H_5COOH \rightleftarrows (C_6H_5COOH)_2$, whence

$$K = \frac{(m_1)^2}{C_2 - m_1} = \frac{\left[\frac{C_1(1 - \alpha)}{k}\right]^2}{C_2 - \frac{C_1(1 - \alpha)}{k}} = \frac{[C_1(1 - \alpha)]^2}{C_2k^2 - C_1k(1 - \alpha)}.$$

Assuming now that the value K is a constant, values of C_1 and C_2 from two experiments (lines 1 and 7) of Table VI are inserted in the equation and the value of the distribution constant k is found to be 0.700.

With this known, the value of m_1, the concentration of simple molecules, can be calculated by the formula $\frac{C_1(1 - \alpha)}{m_1} = k$, and the figures are given in column 5. Column 6 gives the concentration of double molecules $C_2 - m_1$, and column 7 gives the nearly constant values for K.

TABLE VI

Distribution of Benzoic Acid between Water and Benzene at 10°
$K = 0.700$

C_1	C_2	d	$C_1(1 - \alpha)$	m_1	$C_2 - m_1$	$\frac{m_1^2}{C_2 - m_1} = K$
0.0429	0.1449	0.169	0.0357	0.0510	0.0939	0.0277
0.0562	0.2380	0.149	0.0474	0.0677	0.1703	0.0269
0.0823	0.4726	0.125	0.0720	0.1029	0.3697	0.0286
0.1124	0.8843	0.104	0.1007	0.1439	0.7404	0.0279
0.1780	2.1777	0.0866	0.1626	0.2323	1.9454	0.0277
0.2430	4.0544	0.0747	0.2249	0.3213	3.7331	0.0276
0.2817	5.4851	0.0695	0.2621	0.3743	5.1108	0.0274

The literature contains a very considerable number of cases like the above in which distribution experiments have been used to determine dissociation or association or both. Ordinarily, the degree of dissociation has been known through independent conductivity experiments, and the degree of association determined by application of the theory as given above. Thus, Hendrixson (*loc. cit.*) determined the association of benzoic acid and of salicylic acid in benzene and in chloroform. Herz and Fischer[1] and Herz and Lewy[2] have determined the association of acetic acid and chloracetic acid in benzene, toluene, xylene, chloroform, bromoform, carbon disulfide and carbon tetrachloride, using water as the other solvent in each case. Donnan and Garner[3] by the same method found lithium chloride to exist chiefly as double molecules in amyl alcohol.

There have been numerous cases like the above in which distribution experiments have been of use in measuring, with considerable accuracy, the degree of association of certain compounds. The effort, on the other hand, to use the same method of experimentation so as to measure the degree of electrolytic dissociation, has been much less often made and, on the whole, with much less success. This has been due, in considerable part, to the fact that but few compounds are known which meet the requirement of being fairly strong electrolytes (salts, strong bases and acids) and of being at the same time soluble both in water, where the dissociation occurs, and in non-dissociating solvents like the hydrocarbons. There is the further difficulty that, where the above requirements are met, the compound is associated in the second solvent and its degree of association not known with sufficient accuracy to be set into the above formulæ with any great degree of confidence. Where such experiments have been possible, they have led to conclusions as to the degree of electrolytic dissociation which are out of harmony with the results obtained by other methods. Thus Rothmund and Drucker[4] used distribution experiments in investigating the electrolytic dissociation of picric acid in water by measuring its distribution between that solvent and benzene. Algebraic treatment similar to that given above showed that, on the assumption that the acid exists wholly in the form of double molecules when in benzene, its dissociation in water follows the mass law, or Ostwald dilution formula, the dissociation constant being 0.164. This conclusion stands in contradiction to the fact that strong acids do not follow the Ostwald formula, as far as evidence exists based upon their electrical conductivity; the contrary evidence of Rothmund and Drucker is of course weakened by the fact that an assumption as to the association in benzene is involved. Later experiments by Drucker,[5] where tribenzylmethylammonium salts were used, gave a much less satisfactory constant for the distribution ratio when the assumption was made that the electrolytic dissociation followed the Ostwald formula. More extreme results have been found by Schuncke,[6] who noted that hydrogen chloride leaves ether completely and passes wholly into water, and by Hill,[7] who studied the distribution of silver perchlorate between water and benzene, water and toluene, and water and aniline; the salt passes wholly into the water in the first two cases and wholly into the aniline in the third case. In all these cases it is clear that there can be no molecular species common to both phases; what the condition of the distributed compound may be in each phase is not easy to determine.

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[1] *Ber.*, **38**, 1138 (1905).
[2] *Z. Elektrochem.*, **11**, 818 (1905).
[3] *J. Chem. Soc.*, **115**, 1325 (1919).
[4] *Z. physik. Chem.*, **46**, 826 (1903).
[5] *Z. Elektrochem.*, **18**, 562 (1912).
[6] *Z. physik. Chem.*, **14**, 331 (1894).
[7] *J. Am. Chem. Soc.*, **43**, 254 (1921); **46**, 1132 (1924).

Study of Other Equilibria by Means of Distribution Experiments: It will be readily seen that distribution experiments may shed much light on a variety of other chemical equilibria as well as upon association or dissociation. If *x* in Fig. 3 represent a substance whose distribution coefficient between two phases can be determined, and if it is capable of entering into a reversible reaction with a second substance *y* in one of the phases, the constants of this second equilibrium can be easily evaluated from a series of distribution experiments; analysis of the upper phase for its content of *x* will give the concentration of uncombined *x* in the lower phase from the distribution ratio previously determined, and analysis of the lower phase for *x* will give its total concentration as *x* and *xy*, from which the concentration of *xy* follows; since the total concentration of *y* is the amount taken, and its proportion in *xy* follows from knowledge of the composition of that compound, the concentration of uncombined *y* is likewise known, and with *x*, *y* and *xy* known in the lower phase the constants of the equilibrium can be immediately calculated.

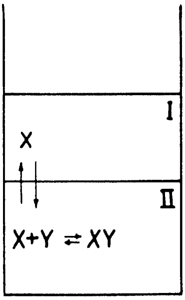

FIG. 3. Distribution Diagram for a Compound Undergoing Combination

In accordance with this principle, Kuriloff[1] has studied the equilibrium

$$\text{naphthol} + \text{picric acid} \rightleftharpoons \text{naphtholpicrate}$$

in benzene solution. Roloff[2] has studied the action of bromine on potassium bromide in forming the polybromide KBr_3, and Jakowkin[3] has studied the formation of similar polyiodides and the interesting case of the hydrolysis of chlorine.

$$Cl_2 + HOH \rightleftharpoons HCl + HClO.$$

Dawson[4] by studying the distribution of ammonia between chloroform and aqueous solutions of copper sulfate was able to show the existence of the compound $CuSO_4.4NH_3$ in the aqueous phase together with certain dissociation products. Farmer[5] has, in like manner, determined the hydrolysis of the barium salt of hydroxyazobenzene by distribution experiments between benzene and water. The method is one of very wide applicability, though it is unquestionably true that in many instances the conclusions are complicated by the fact that there are several equilibria occurring in each phase.

Nernst (*loc. cit.*) has given the most generalized form in which equilibria may be studied by means of distribution experiments. Let a two-phase system be considered, in each phase of which an equilibrium exists according to the following scheme:

$$n_1A_1 + n_2A_2 + \cdots \rightleftharpoons n_1'A_1' + n_2'A_2' + \cdots,$$

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[1] *Z. physik. Chem.*, **25**, 419 (1898).

[2] *Z. physik. Chem.*, **13**, 341 (1894).

[3] *Z. physik. Chem.*, **20**, 19 (1896); **29**, 613 (1899); *Ber.*, **30**, 518 (1897).

[4] *J. Chem. Soc.*, **89**, 1666 (1906).

[5] *J. Chem. Soc.*, **79**, 863 (1901).

in which A_1, A_2, A_1' and A_2' represent molecular species and n_1, n_2, n_1' and n_2' represent the stoichiometrical coefficients; and let C_1, C_2, C_1' and C_2' represent the concentrations of these molecular species in the one phase at equilibrium, and c_1, c_2, c_1' and c_2' the concentrations in the second phase. The mass-law equations representing these equilibria in the two phases will be

$$\frac{C_1^{n_1}C_2^{n_2}}{C_1'^{n_1'}C_2'^{n_2'}} = K,$$

$$\frac{c_1^{n_1}c_2^{n_2}}{c_1'^{n_1'}c_2'^{n_2'}} = K_1.$$

Each of the molecular species is distributed between the two phases, which fact is represented by a series of distribution ratios

$$\frac{C_1}{c_1} = k_1, \quad \frac{C_2}{c_2} = k_2, \quad \frac{C_1'}{c_1'} = k_1', \quad \frac{C_2'}{c_2'} = k_2'.$$

By division of the first two equations, an equation results:

$$\frac{K}{K_1} = \frac{k_1^{n_1}k_2^{n_2}}{k_1'^{n_1'}k_2'^{n_2'}}.$$

It follows therefore that, if the equilibrium constants of a reaction occurring at a fixed temperature in a given phase are known and if, also, the distribution constants of all the molecular species are known, the equilibrium constant in the second phase at that temperature can be calculated. The conclusion is of course valid whether the two phases be liquids or whether one of them be a gaseous phase.

Amorphous Phases: The substitution of an amorphous body for one of the liquid phases should have no effect upon the validity of the distribution law. It is customary to look upon such amorphous bodies as liquids of high viscosity, which property should in no wise interfere with the establishment of a true equilibrium, although it may lengthen the time required for the attainment of equilibrium. Such a case has been studied by Küster;[1] ether distributes itself between water and the amorphous substance caoutchouc as shown in Table VIII.

The application of the distribution law to cases involving a colloidal substance is simple in principle, but the interpretation of the results is by no means simple. The adsorption of dissolved substances from solutions upon colloidal bodies is obviously a case of distribution of a substance between two phases. Indeed, a common method of writing the adsorption isotherm, $\frac{C^n}{C} = K$, is formally identical with the distribution law as it has been used for cases in-

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[1] *Z. physik. Chem.*, 13, 452 (1894).

TABLE VIII

DISTRIBUTION OF ETHER BETWEEN CAOUTCHOUC AND WATER AT 18°

C_k	C_w	C_k/C_w	$\sqrt{C_k}/C_w$
3.85	1.24	3.10	1.58
7.96	2.34	3.41	1.21
16.14	4.26	3.79	0.94
20.12	5.07	3.97	0.88
24.49	5.66	4.33	0.87
28.82	6.37	4.40	0.83
31.43	6.99	4.50	0.80
35.09	7.40	4.74	0.80
38.09	7.93	4.80	0.78
49.18	9.18	5.36	0.76

The first column indicates the grams of ether per 100 cc. of the caoutchouc phase and the second column the number of grams in the same volume of the aqueous solution. The ratio of these values, given in column three, gives figures with a decided trend, but the substitution of the square root of the values of C_k in the formula (Column 4) gives values which are not far from a constant; the conclusion is therefore that, in the caoutchouc phase, the ether is predominatingly bimolecular.

volving association; but where adsorption from water occurs, for example, the exponent n must be applied to the *water* phase, and is of the order of magnitude of 1/5 or 1/10. Reasoning such as has been used in distribution experiments would therefore lead to the astounding conclusion that the distributed phase has only a fraction of the molecular weight in the colloid which it possesses in water. Since compounds usually possess their minimum molecular weight in water, the conclusion that they have still lower molecular weights in the colloid phase is untenable; rather, it seems wiser to conclude that surface effects have here a predominating influence because of the huge surfaces possessed by colloids, and that the distribution law is masked by these greater influences.

The Process of Extraction: Probably the commonest use to which the distribution principle is put in ordinary laboratory practice is the process of extraction. Organic compounds in particular are easily and completely removed from inorganic materials by extracting the aqueous solution with ether or similar organic solvent; the distribution ratio of most organic bodies is largely in favor of the ether phase, whereas that of inorganic bodies is almost wholly in favor of the aqueous phase, so that repeated extraction with ether will give a nearly perfect separation in the majority of instances. It is frequently possible to increase the ratio in the desired direction by addition of another compound which depresses the dissociation of the substance being extracted; an organic acid of moderate strength for example can be most advantageously extracted from water after addition of a strong inorganic acid, which by its excess of hydrogen ion will convert the organic acid chiefly into undissociated molecules, which are soluble in the ethereal phase whereas the ions are not. An organic base, by the same reasoning, is most easily extracted *in the presence of a strong inorganic base.* The addition of neutral bodies such as salts will also in many cases lower the solubility of the organic compound in water (the so-called salting-out effect) and thus favor the extraction by the ether.

In the majority of extraction processes there has been no extended study as to distribution constants, degree of association, dissociation or combination, but the most appropriate extracting agent has been found by the method of trial. There is, however, in all cases, a general principle of great value which can be applied in determining the best method of extraction with a given quantity of extracting liquid, for it can be shown that extraction by means of several fractions of the liquid is more complete than if the whole liquid be used in a single extraction. A simple example will make this point clear. Let a liter of an aqueous solution be considered, holding 100 gms. of an organic compound, and let one liter of ether be considered as the extracting liquid; further, let the distribution ratio of the compound in ether and water be 2. It is apparent that if the whole sample of ether be used in a single extraction of the liquid, the amount dissolving in the ether will be 66.7 gms. If on the other hand the extraction be carried out with two 500 cc. samples consecutively, 50 gms. will be extracted on the first treatment, and 25 gms. on the second, raising the total yield from 66.7 gms. to 75 gms. If now the extraction be conducted with ten 100 cc. samples of ether, the amounts extracted by the successive operations will be 16.67 gms., 13.89 gms., 11.58 gms., 9.65 gms., 8.03 gms., 6.70 gms., 5.58 gms., 4.65 gms., 3.88 gms., 3.23 gms., making a total of 83.86 gms. In the majority of instances, the distribution ratio is far more favorable than the 2 : 1 ratio here assumed, so that extraction approaching 100 per cent can frequently be effected with comparatively few operations. In all cases, however, extraction by fractional parts is more efficient.

If the distribution ratio is known for the materials contained in a given extraction, it is possible to derive a generalized formula which will show the amount still unextracted after a given number of operations.[1] Let W cc. of a solution containing x_0 gms. of a substance be repeatedly extracted with L cc. of a given solvent. After the first extraction, let x_1 represent the number of grams remaining unextracted. The concentration in the extracting phase will then be $\frac{x_0 - x_1}{L}$ and in the original solution $\frac{x_1}{W}\cdot$ The distribution ratio K will then be, by definition,

$$\frac{x_1}{W} \div \frac{x_0 - x_1}{L} = K,$$

whence

$$x_1 = KW \times \frac{x_0 - x_1}{L} = x_0 \frac{KW}{KW + L}\cdot$$

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[1] Taken from Herz, Der Verteilungssatz, Stuttgart, 1909, p. 5.

After a second extraction x_2 gms. remain in the original solution; the equation takes then the corresponding form

$$x_2 = x_1 \frac{KW}{KW + L}.$$

If now the former value for x_1 be substituted in the equation,

$$x_2 = x_0 \frac{KW}{KW + L} \cdot \frac{KW}{KW + L} = x_0 \left[\frac{KW}{KW + L} \right]^2.$$

Putting the equation now in a generalized form, after the nth extraction, the residual quantity x_n is as follows:

$$x_n = x_0 \left[\frac{KW}{KW + L} \right]^n.$$

Inspection of this generalized formula shows that for the residue x_n to be very small, the distribution constant K should also be small (i.e., the distribution ratio toward the phase being extracted should be small), and the number of extractions, n, should be large.

Temperature Coefficients: A change in the distribution ratio with change in temperature may be anticipated from the fact that the solubility of a substance ordinarily changes with the temperature and that the changes are usually of different magnitude in the two different solvents used. Forbes and Coolidge[1] have derived the temperature coefficient of the distribution ratio of succinic acid in water and ether from solubility data, and obtain a calculated coefficient of 0.0258 per degree, in good agreement with the experimental figure 0.0255. Hantzsch and Sebaldt[2] find that the distribution ratio of acetic acid between water and ether varies only from 2.031 at 0° to 2.19 at 25°, and that of mercuric chloride under the same conditions from 0.391 to 0.429; between water and toluene[3] the distribution ratio of acetone falls from 2.09 at 0° to 1.95 at 30°, and that of mercuric chloride in the same solvents from 12.35 at 0° to 11.25 at 50°. These are all rather small changes, and have led to the loose but useful generalization that temperature changes have but small influence upon distribution ratios. This must frequently be the case, since the distribution ratio alters only with the *difference* between the solubility ratios. In cases, however, where the temperature coefficients of solubility in the two phases are widely different, as where the solubility coefficient is positive in one solvent and negative in the other, large changes in the distribution ratio must result. The same condition will result if any equilibrium is more largely affected by temperature change in the one phase than in the other, whether the reactions be those of dissociation, association, or compound formation. Thus Hantzsch (*loc. cit.*) and his co-workers found that the distribution of ammonia and amines between water and water-like compounds such as glycerine or ether on the one hand, and hydrocarbons or similar liquids on the other hand, shows a very pronounced temperature coefficient, which they ascribe to the formation of hydrates or similar compounds.

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[1] *J. Am. Chem. Soc.*, **41**, 150 (1919). See also MacDougall, *ibid.*, **41**, 1718 (1919).

[2] *Z. physik. Chem.*, **30**, 258 (1899).

[3] Hantzsch and Vogt, *Z. physik. Chem.*, **38**, 705 (1901).

On theoretical grounds it may be assumed that pressure changes also affect distribution ratios between liquid phases, since solubility is affected by the pressure; but such effects must be of exceedingly small magnitude, and have not as yet been noted.

Limitations in Application of the Distribution Law: It has been pointed out that the strict application of the distribution law in gas-liquid systems is limited to dilute systems. The same limitation applies when the phases are two liquids. There is also here the additional limitation that the two liquid phases shall not change their mutual solubility with change of concentration of the distributed phase. Further, corrections in the formula are necessary for each equilibrium affecting the distributed compound in either phase, whether of dissociation, association or chemical combination. In view of these numerous correction factors, which frequently cannot be applied with exactness because of our lack of knowledge of the equilibria concerned, it is not surprising that absolute constancy in the distribution ratio between two liquids has rarely, if ever, been found. It is obvious, therefore, that the distribution principle is interwoven into the problem of the condition of dissolved bodies, concerning which our knowledge is far from complete.[1] Because of this interrelation it is the part of wisdom to accept the distribution law tentatively as valid and make use of it in gaining information as to the nature of the changes which a body undergoes upon being dissolved in a liquid.

Distribution in the System Liquid-Solid

In extending the distribution law to systems containing a solid phase, the only new point of view necessary concerns a solid body as a solvent. A more complete presentation of this topic will follow in the discussion of the phase rule. For the present purpose it is sufficient to look upon a solid solution as a substance as truly homogeneous as a liquid solution, but with the physical attributes of the solid condition instead of the liquid condition. The distribution ratio of a substance between a solid and a liquid phase will be the ratio of its solubilities in the solid and liquid. Solids do not so frequently show solvent properties as do liquids; thus ice is not a solvent for countless compounds which dissolve freely in liquid water; but a certain number of other solids have been found to possess this property, and, in certain of such cases, the distribution law has been tested. Table IX gives the results of Beckmann's[2] experiments on the distribution of thiophene between liquid benzene and solid benzene and Bruni's[3] work on piperidine in the same two solvents.

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[1] See Hantzsch and Sebaldt, *loc. cit.;* Hantzsch and Vogt, *loc. cit.;* Georgievics, *Z. physik. Chem.*, **84**, 353 (1913) and **90**, 47 (1915); Smith, *J. Phys. Chem.*, **25**, 160, 204 and 605 (1921).

[2] *Z. physik. Chem.*, **22**, 612 (1897).

[3] *Gazz. chim. ital.*, **28**, 1, 259 (1898).

The columns headed C_l represent the percentage composition of thiophene or piperidine in the liquid benzene and those headed C_S represent their concentration in the solid benzene. The temperatures are the freezing point temperatures of the benzene solutions, slightly lower than the freezing point of pure benzene (5.48°).

TABLE IX

DISTRIBUTION OF THIOPHENE AND OF PIPERIDINE BETWEEN LIQUID BENZENE AND SOLID BENZENE

Thiophene			Piperidine		
C_l	C_S	C_S/C_l	C_l	C_S	C_S/C_l
1.22	0.48	0.396	0.553	0.072	0.13
2.28	0.99	0.434	1.37	0.155	0.11
2.87	1.29	0.459	2.57	0.216	0.09
3.42	1.49	0.437	3.21	0.313	0.10
4.50	1.87	0.414	4.20	0.499	0.12
6.44	2.66	0.413	4.68	0.615	0.13
11.20	4.38	0.391			
16.60	6.29	0.379			

From the constancy of the ratios C_S/C_l, it is apparent that both thiophene and piperidine possess the same molecular condition in solid benzene as in its liquid form. It will also be noted that the solubility of thiophene in solid benzene is very considerable, amounting to about 4/10 of its solubility in the liquid, it is evident therefore that purification of benzene from thiophene by the method of crystallization is beset with difficulties. Iodine has also been found[1] to have a relatively high solubility in solid benzene and to possess normal molecular weight in both the liquid and solid solvent.

In the above examples, the same substance figures as solvent in both the solid phase and the liquid phase; the distribution follows the same principle, however, when the solid phase is of different composition. As an example, there are given in Table X figures on the distribution of thallous nitrate between solid potassium nitrate and an aqueous solution, as determined by Fock.[2] It is of course necessary that the solution be saturated with the potassium nitrate in order that the solid phase may be present.

The concentration of this salt, expressed in moles per liter is given in the first column. The concentration of the thallous nitrate in the liquid phase (C_l) is given in column 2 and its concentration in the solid potassium nitrate in column 3 (C_S), both expressed in moles per 100 moles of solution, the ratio C_l/C_S given in column 4 is satisfactorily constant, and again shows that the molecular condition of the thallous nitrate is the same in both solvents. Ionization has been reduced to a minimum in the aqueous phase by the common ion from the large excess of potassium nitrate.

DISTRIBUTION IN OTHER SYSTEMS

Where two phases are under discussion, the possibilities as to combinations in which distribution might occur are the following: gas-liquid, liquid-liquid,

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[1] van't Hoff's Lectures, **II**, 75.

[2] *Z. Krystall.*, **28**, 337, *Zentral.*, 1891, I, 710, taken from Lewis, Physical Chemistry, 1916, p. 344.

TABLE X

DISTRIBUTION OF THALLOUS NITRATE BETWEEN SOLID POTASSIUM NITRATE AND AQUEOUS SOLUTION

Conc. KNO_3	C_l	C_S	C_l/C_S
3.2658	0.3238	2.77	0.117
3.2944	0.1869	1.78	0.105
3.2981	0.0663	0.57	0.116
3.2851	0.0231	0.20	0.116
3.2515	0.0089	0.08	0.111

liquid-solid, gas-solid, solid-solid. Two gaseous phases are impossible, since all gases are completely soluble. Three of these five combinations have been discussed above; the discussion of the remaining two may be made brief. Distribution between a gaseous phase and a solid phase of course requires that the distributed compound be itself a gas, and capable of dissolving in the solid. That such cases occur is in accord with the well-known diffusion of hydrogen through platinum or palladium, but the solubilities are usually of a low order; when large apparent solubilities are found, the result is frequently to be attributed to adsorption upon the surface of the solid, and results are obtained which are not easily interpreted in terms of the distribution law. A number of interesting cases have been investigated by Sieverts and his co-workers,[1] by whom the solution of several gases in common metals was quantitatively examined. The figures for the solubility of hydrogen in nickel are given below.

TABLE IX

SOLUBILITY OF HYDROGEN IN 26.97 GMS. NICKEL

1st Series: Temp. = 923°			2d Series: Temp. = 822°		
Pressure in Cm. of Hg	Cc. of H_2 Dissolved	$\frac{\sqrt{p}}{m}$	Pressure in Cm. of Hg	Cc. of H_2 Dissolved	$\frac{\sqrt{p}}{m}$
764	2.63	10.5	764	2.20	12.6
663	2.50	10.3	660	2.08	12.4
584	2.39	10.1	583	1.93	12.5
448	2.06	10.3	529	1.86	12.4
319	1.62	11.0	447	1.71	12.4
164	1.11	11.5	318	1.41	12.7
129	0.98	11.6	165	1.01	12.7
			132	0.89	12.9
			88	0.72	13.0
			52	0.50	14.4

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[1] *Z. physik. Chem.*, **60**, 129 (1907), **68**, 115 (1910); *Ber.*, **42**, 338 (1909), **43**, 893 (1910), **45**, 221 and 2576 (1912).

In these experiments, as in most others in which a gas is dissolved by a solid, it appears that the solubility is not directly proportional to the pressure, as would be the case if Henry's law expressed the conditions, but is proportional to the square root of the pressure; as interpreted previously, this indicates that the gases in the solid solution have one half the molecular weight which they possess in the gaseous condition, that is, that hydrogen and other elementary gases are present in monatomic condition in the solid phase. An equally simple interpretation for the case of sulphur dioxide in molten copper is not available. The difficulty was elucidated by Stubbs[1] who showed that interaction with the copper occurs.

The solubility or insolubility of a given gas in a given metal has naturally a very important bearing upon the use of the metal as a catalyst in reactions in which the gas takes part; Sieverts gives the following classification of cases studied by him:

nitrogen: not dissolved by metals except by iron and aluminum with the formation of nitrides.
carbon dioxide: insoluble in copper.
carbon monoxide: soluble in nickel; insoluble in copper.
oxygen: soluble in (molten) silver.
sulfur dioxide: soluble in (molten) copper.
hydrogen: soluble in copper, nickel, iron, palladium, insoluble in cadmium, thallium, zinc, lead, bismuth, tin, antimony, silver and gold.

It will be shown, however, in Chapter XV that it is the adsorbed gas rather than the dissolved gas which is really important in catalytic work.

For solid-solid systems the available data are meager; although two solids may frequently show mutual solubility, which will be discussed under the phase rule, the equilibria are usually attained only after long intervals, and independent analyses of the phases are not easily made. For these reasons application of the distribution law has rarely been attempted.

When three-phase systems are considered, the distribution law is still applicable. The simplest application would be when the gaseous phase over two liquid phases is taken into the calculation. It is apparent however that with increase in the number of phases the possibilities as to association, dissociation and chemical combination are likewise increased, and the application of the distribution law becomes increasingly difficult.

THE PHASE RULE

The most useful generalization relating to the physical and chemical reactions which occur in heterogeneous systems is the phase rule of Willard Gibbs.[2] Published in a journal not widely read and developed in a mathematical fashion, its fundamental value was not at once recognized. It is owing to the subsequent adoption of the phase rule by Roozeboom, Ostwald and van't Hoff that it has become generally known to chemists and physicists as a principle of the widest applicability, of the highest value in the classification of heterogeneous equilibria and of the greatest reliability in the settlement of disputed points; van't Hoff made use of the rule in many of his published investigations, Roozeboom made it the basis of his monumental monograph,[3] Die heterogenen

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[1] *J. Chem. Soc.*, **103**, 1445 (1913), *Proc. Chem. Soc.*, **29**, 225.

[2] Gibbs, *Transactions Connecticut Acad.*, 1874-1878, also in Gibbs' Collected Scientific Papers, Longmans, Green and Co., 1906.

[3] Roozeboom, Die heterogenen Gleichgewichte, Braunschweig, 1901 et seq.

Gleichgewichte, and Ostwald adopted it as his basis of classification in his Lehrbuch.[1] Roozeboom had previously been making use of the phase rule in his investigations beginning as early as 1884 to 1887,[2] at the suggestion of van der Waals. It has since this time come into very general use, and has the advantage over others of our commonly accepted generalizations in that it contains no assumptions based upon theory, such as the molecular hypothesis, the kinetic theory, theories of constitution of matter or of chemical reaction, and is therefore not subject to revision or rejection as our views of these matters may change.

In order to appreciate the importance of Gibbs' generalization, it is necessary to have an idea of the type of phenomena with which the phase rule is concerned. In a general way it may be stated that the effect of changing temperature, pressure or concentrations in any heterogeneous system would have to be considered a special problem for each system investigated were it not for the phase rule; by its means, however, the effect of these changing conditions can be shown to follow a definite rule for all systems. A few instances will illustrate the point. Three open flasks may be taken, containing respectively pure water, a dilute solution of hydrochloric acid and a dilute solution of sodium chloride; if these three liquids be heated, their behavior will be entirely different. The water will undergo a steady rise of temperature until its boiling point of 100° is reached, at which point the liquid will boil away without change of temperature until the flask is dry. In the second case, the liquid will begin to boil at some temperature not far from 100° but the temperature will still continue to rise and the solution become more and more concentrated with respect to hydrochloric acid until a temperature of 110° is reached, at which point the liquid will continue to boil without change of temperature or of composition until this flask also is dry. In the third case the liquid will also begin to boil at a little above 100°, and again the temperature will rise until, at about 107°, solid sodium chloride begins to precipitate; the temperature will then remain constant while the remainder of the water boils off, leaving the dry salt behind. The widely different behavior of these three solutions has of course long been known; but it remained for the phase rule to show that the three cases could all be interpreted in terms of a single law. In like fashion, if the three solutions were subjected to conditions which would withdraw heat from them, the first would show a constant temperature only once during the withdrawal, the third twice and the second a number of times—explicable again in terms of the same phase rule. In short, a very large number of previously unrelated phenomena, dealing with changes involving several phases, have been clearly and intelligibly related by means of the phase rule, and predictions as to countless reactions not yet investigated may be made with complete safety.

The Phase Rule: The phase rule of Gibbs is stated in terms of the number of phases present in a system at equilibrium, the number of components from which the system can be built up, and the number of conditions (pressure, composition or temperature) which may be varied without causing a change in the number of phases. In words the statement of the relationship is somewhat cumbersome, but it may be very simply expressed by the equation

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[1] Ostwald, Lehrbuch der Allgemeinen Chemie, 2d Edition, Leipzig, 1903.

[2] Die heterogenen Gleichgewichte, I, p. 7.

$$F = C - P + 2,$$

in which C stands for the number of components of the system, P the number of phases present, and F the degree of freedom, or the variance, of the system. Before passing to the application of this rule to any system under observation, it is necessary that each of the terms used, either in a verbal statement of the rule or in the equation, should be accurately defined and thoroughly understood. The list includes the terms equilibrium, phase, component, and degree of freedom.

Equilibrium: An equilibrium exists in any system under a fixed set of conditions when the parts of the system do not undergo any change of properties with the passage of time, provided (which is the crux of the statement) that the parts of the system have these same properties when the same conditions are again arrived at by a different procedure. It is this provision which makes possible the distinction between stable equilibrium and metastable equilibrium; in both cases the system may be capable of maintaining itself perhaps indefinitely without change, but in the case of metastable equilibrium an alteration in the method of producing the system will give us an entirely new set of properties. As an example of this distinction, let a vessel of water be considered which is cooled slowly and carefully to a temperature of − 1°; with care such a system may be maintained as long as desired, and will consist of water of a certain density and vapor of a certain pressure It appears then that the system is in equilibrium. Again, ice at some low temperature may be carefully warmed to − 1°, when it will have a fixed density and a fixed vapor pressure somewhat lower than that of the former system; equilibrium appears to exist in the second case also. The distinction lies in the fact that this second system may also be produced by cooling water, while the first can never be produced by warming ice; ice and vapor at − 1° may then be considered a system in stable equilibrium, while water and vapor at − 1° are in metastable equilibrium.

In making use of the phase rule, it is a matter of the most fundamental importance to remember that it applies to systems in true equilibrium and only when they are in true equilibrium. If the mathematical application of the rule shows, in some of the cases to be studied, that only a certain number and class of phases can be present at equilibrium, the conclusion of course is not justified that no other number of phases can be present; if the system is not in temperature equilibrium (i.e., if different parts of it have different temperatures) or if the phases are out of equilibrium (i e , the phase reactions have not been completed), the system may be quite different from that which would be deduced by the phase rule. Practical experience with conventional ice water will convince anyone that it is possible to have ice, water and vapor in a tumbler many degrees above zero, and the experience does not constitute a contradiction of the phase rule; it indicates only that we frequently drink the liquid before equilibrium has been attained. Nor does the phase rule give any indication of the rapidity or slowness with which a given equilibrium is reached or how it is most easily produced; it is severely limited to an exact statement of the existing conditions when equilibrium has been attained, in the sense in which equilibrium has been defined above.

Phases: The term phase has for some time been a part of the nomenclature of elementary chemistry; the concept is simple and easily grasped. A phase is any part of a system, which is homogeneous throughout; it is bounded by a surface and is mechanically separable from the other parts of the system. Such a phase is necessarily in one of the three physical states of aggregation, gaseous, liquid or solid. Since all gases are found to be mutually soluble, that is, to pass into a homogeneous condition, it follows that there can be only a single gaseous phase in any system under consideration; with liquids complete solubility is by no means always the case, and there may therefore be several liquid phases present in certain systems, and the same is true for solids. However many liquids or solids may have been formed under varying conditions from the components of a given system, in no case has the number of liquid phases coexisting at equilibrium been found greater than the number of the components in the system, and the number of coexistent solid phases at equilibrium cannot exceed the number of components by more than two, as will be shown later. With regard to the composition of the gaseous, liquid and solid phases, the phase rule makes no assumption as to their classification as elements, compounds or solutions, and distinguishes only between phases of fixed composition and those of variable composition; but, if the customary chemical method of classification be used, it may be stated that any phase, whether gaseous, liquid or solid, may be composed of an element, a compound, or a solution of elements or compounds, since all these forms are homogeneous. Mixtures only are excluded, since, by definition, a mixture is heterogeneous and therefore composed of at least two phases. Finally it should be pointed out that a phase need not be continuous; the gaseous phase, because of the diffusibility of gases, is generally continuous in any system, and the liquid phase because of the fluidity of liquids is usually so, though it may of course be broken into droplets by agitation; solids however are commonly present as discontinuous fragments. Continuity is excluded from the definition of a phase, since discontinuity brings about no change except one of surface, which will be discussed in the paragraph on variables. Gibbs[1] in introducing the term phase states that it refers "solely to the composition and thermodynamic state of any body without regard to its quantity or form."

Components: The concept of the components is frequently less easily grasped than the other necessary concepts by those taking up, for the first time, the study of the phase rule. This is, perhaps, because of a double use to which we put the term. It is necessary to derive, in the first place, the

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[1] Scientific Papers, p. 96.

number of components, in order to have a numerical value to substitute for the term C in the phase-rule equation; it is also necessary to name the ***individual components*** in terms of which the composition of the various phases is to be expressed. The number of components must have a perfectly definite value, derivable in a systematic manner, and subject to no arbitrary desire on the part of the investigator. The individual components on the other hand, while limited in number as stated, may be chosen at will within certain limits, as will be shown; here, there is a certain freedom of choice not permissible in the former instance.

The *number of components* of a system at equilibrium is defined as the smallest number of independently variable constituents by means of which the composition of each phase may be mathematically expressed. In accordance with this definition it is possible, though it is not the usual practice, to determine this number without any reference to what the individual components may be. This may be done, for example, by determining the value of C in the equation when the other variables (F and P) are known. It is also possible to arrive at the number empirically, from analysis of all the phases present; if they are all of the same composition (under varying conditions), the system is of one component, if the phases present can be produced from any two phases, the system is of two components, while if more phases are necessary to express the composition of any one, the number of components is represented by that number of phases. More commonly, however, the number of components is deduced from knowledge as to the physical or chemical changes which the system undergoes. Thus if the decomposition of calcium carbonate by heat is being studied, it is known that the phases present consist of a gaseous phase composed chiefly of CO_2 with whatever traces of $CaCO_3$ and CaO are capable of volatilization, and two solid phases, CaO and $CaCO_3$. It is clear that from two components, most simply CO_2 and CaO, the composition of each of these three phases may be expressed in the usual terms of percentage by weight, or in terms of other units; a smaller number (one) is incapable of doing this. In expressing the composition of the solid CaO, the amount of CO_2 is zero; neither zero values nor negative values however are excluded by the definition given. If we now consider what *individual components* shall be chosen in discussing this system, it would be wisest to choose CO_2 and CaO, since minus quantities will then not enter into any statement of composition and graphical representation will be most simple; but other choice may be made, as illustrated below.

Components chosen	$CaO + CO_2$	$CaCO_3 + CaO$	$CaCO_3 + CO_2$
Per cent composition of gaseous phase	0% CaO + 100% CO_2	156% $CaCO_3$ − 56% CaO	0% $CaCO_3$ + 100% CO_2
Per cent composition of quick-lime phase	100% CaO + 0% CO_2	0% $CaCO_3$ + 100% CaO	144% $CaCO_3$ − 44% CO_2
Per cent composition of carbonate phase.	56% CaO + 44% CO_2	100% $CaCO_3$ + 0% CaO	100% $CaCO_3$ + 0% CO_2

It happens that, in this instance, each phase is of invariant composition, but in some two component systems the composition of some phase, namely, a solution, may vary from 0 per cent of component A and 100 per cent of component B to 100 per cent of A and 0 per cent of B.

The number of components of a system may differ also with the conditions under which its equilibria are being studied. Thus, water is regarded as a one-component system because, under the ordinary conditions of experimentation, the three phases found (ice, liquid and vapor) may all be expressed as composed of water alone; but, if temperatures are raised until the dissociation of water has begun, according to the equilibrium

$$2H_2 + O_2 \rightleftharpoons 2H_2O,$$

it would no longer be possible to express all possible compositions in terms of water; for, if excess hydrogen or oxygen be introduced, the composition of the vapor phase can be expressed only in terms of two components, hydrogen and oxygen, whose concentrations can be independently varied. *The number of components* then, while always definite, may vary with the condition of the system, and is arrived at in accordance with the definition given; the *individual components* may be chosen according to convenience from among the substances taking part in the equilibrium.

It is upon the basis of the number of components that systems are classified for phase-rule study as one-component systems, two-component systems, etc.

Degree of Freedom (Variance of a System): In the application of the phase rule, the independently variable conditions which are taken into consideration are three in number—*temperature, pressure,* and *composition.* This restriction of the types of independent variables to three is of course arbitrary; usually the effects of gravitation, of electrical condition, of surface energy and of light absorption are purposely excluded. It is necessarily true that these variables may have an effect upon the equilibrium existing between various phases, but in large numbers of cases their effect is negligibly small; in the cases where their effect is large, the phase rule as here given affords but small help, as in the field of colloid chemistry, where surface energy is the most influential factor. If only these three variables are considered, it follows that when these three are known the system may be regarded as defined; that is, a complete statement of the properties of each phase is implied by the statement of the three variables. Thus, to state that a gaseous system contains 50 per cent each of carbon dioxide and nitrogen at 20° C. and 760 mm. pressure of mercury, defines the system in that any other sample of these gases made up according to the same conditions will be identical with the first in all properties except mass.

It is however not necessary in all cases to fix as many as three conditions in order to define the system under observation, and it is precisely the number of these variables which must be arbitrarily fixed, in order completely to define the system, that is called the *degree of freedom* of that system. The mixture of gases mentioned above is obviously a system with three degrees of freedom, since a statement of a temperature, a pressure and a concentration were necessary; if the system to be defined is a saturated solution of sodium chloride with excess solid and vapor, we need mention only the desired temperature and pressure (two degrees of freedom), while for a system of ice, water and vapor no further statement of condition is necessary. The specific application of this principle will appear in the examples to be studied; it will suffice for the present to state the customary nomenclature, which is to describe systems with no degree of freedom as *invariant*, those with one degree of freedom as *univariant*, those with two as *bivariant*, and so on for other multivariant systems. The possibility for a system to have a variance greater than three, where only temperature, pressure and composition are the variables, lies in the fact that, for multicomponent systems, knowledge of the concentration of more than one component is necessary in order to state the composition: thus, in a solution containing three components, the composition with respect to two must be stated before the composition of the solution is known.

Further Restrictions: In the application of the phase rule equation, it frequently happens that there are certain additional restrictions which must be taken into account in the equation. The mathematical effect of any such additional restriction is to decrease by one the value of the terms upon the right hand of the equation $F = C - P + 2$, which means necessarily to reduce the number of degrees of freedom by one. This would be the same in effect as decreasing the number of components by one, and is usually viewed in that manner. An illustration will make the practice clear. If the substance under investigation were ammonium chloride, which decomposes according to the equation

$$NH_4Cl \rightleftharpoons NH_3 + HCl,$$

it is clear that the system is a two-component system since, if all possible relationships in the gaseous phase are studied, varying amounts of NH_3 and HCl must be added, and the composition of that phase cannot be expressed by fewer components than those two. But, let the restriction now be imposed that the NH_3 and HCl shall always be in the molecular ratio 1 : 1; i.e., that no excess NH_3 or HCl shall be added; the system may under these conditions be treated literally as a one-component system since the composition of either phase may be regarded as NH_4Cl, and will have the number of degrees of freedom corresponding to a one-component system. Again, in the study of a liquid which undergoes the critical phenomena at its critical temperature, it might appear, since we have only two phases present, that the system is univariant, since substitution of 1 for C and 2 for P gives $F = 1$; actually however the statement that the substance is undergoing the critical phenomena imposes an additional restriction included in the definition of the critical state, which is that the two phases shall be identical. This restriction reduces the degrees of freedom by one and indicates that the system is invariant, which means that the critical phenomena occur only at a fixed and unvarying temperature and pressure for a given liquid. This is of course in accord with the facts; the omission of the added restriction would lead to the entirely false conclusion that the system is univariant and that the experimenter might therefore determine for himself at what temperature or at what pressure the liquid might be made to pass into the critical condition. Indeed, it is just this restriction which differentiates a one-component liquid at its boiling point, which is a state of univariant equilibrium and the temperature of which can be altered by changing the pressure, from the same liquid at its critical temperature, when the system is invariant.

Derivation of the Phase Rule: With the various terms of the phase rule discussed, a brief statement of its method of derivation may be made. The rigorous thermodynamic derivation which Gibbs made is abstract and difficult; the reader is referred to Gibbs' papers (*loc. cit.*) for details, or to other extended treatises.[1] The following is not given as a rigorous derivation, but is nevertheless useful in showing in a general way the method of derivation which Gibbs used.

It has previously been shown that the degree of freedom (F) of a system is the number of variables which must be arbitrarily fixed in order to define the system. It follows simply enough that the number of such variables must be equal to the total number of variables of the system minus the number of variables which are defined by the system itself; that is,

$$F = (\text{total variables of the system}) - (\text{defined variables}).$$

A numerical statement of these two terms in the equation, if it can be put in such fashion as to include only the number of phases and number of components, will give the phase rule equation.

The total number of variables can easily be calculated. As stated above, they may be the variables of temperature, of pressure and of composition. There can be but one temperature and one pressure throughout a system at equilibrium, so that the temperature and pressure variables total two. The composition variables however may be numerous. In each phase the composition may vary, and within each phase the number of variations in composition is equal to the number of components less one, i.e., to $(C - 1)$, since for two components we may vary the percentage composition with respect to one of them and derive the second by difference, and for three components by similar reasoning we may vary two. The total number of composition variables in all the phases is therefore $P(C - 1)$, and the total number of variables of all kinds is greater by the two variables of temperature and pressure, so that the total number of variables to be set in the equation above is $P(C - 1) + 2$.

In order to calculate the second term, the number of variables defined by the system itself, Gibbs introduced the concept of the thermodynamic or chemical potential which each component possesses, and which is the intensity factor of the chemical energy of that component. In a system at equilibrium this chemical potential of each component must be the same in each phase, just as for thermal equilibrium the temperature, which is an intensity factor, must be the same in all parts. The potential of a given component in a given phase is a function of the temperature, the pressure and the composition of that phase and an equation exists relating the potential to those three variables.[1] A similar equation exists for this same component in each other phase, giving a number of equations equal to P; but since the potential is the same in each case, it follows mathematically there will be only $P - 1$ independent equations for that component. The fact that these equations may have a form and value unknown to us is of no importance; the essential is that there are $P - 1$ relationships which actually define the potential of that component in the system. Since what is true for one component is true for all, there are $C(P - 1)$ relationships existing in the system which define the chemical potential of all the components, and hence define the equilibrium.

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[1] Roozeboom, Die heterogenen Gleichgewichte, I, 21; Partington, Thermodynamics. D. van Nostrand, 1924.

It remains only to insert these two terms in the equation given above:

$$F = [P(C - 1) + 2] - [C(P - 1)] = C - P + 2.$$

SYSTEMS OF ONE COMPONENT

When a system consisting of a single component is considered, it follows, by substitution in the phase-rule equation, that it is bivariant if it exists in but one phase, univariant if it exists in two phases, and invariant if it exists in three. Since the number of phases cannot be less than one, the degree of freedom of such a system cannot exceed bivariance. The independent variables are limited to the pressure and the temperature, since all phases are alike in composition.[2] If it is assumed that such a system can have but one vapor phase, one liquid phase, and one solid phase, the following classification may be made, in which the symbols V, L, and S stand respectively for vapor phase, liquid phase and solid phase:

Bivariant	Univariant	Invariant
V	$L + V$	$S + L + V$
L	$S + V$	
S	$L + S$	

More than a single vapor phase cannot be present, since gases or vapors are always mutually soluble, and more than a single liquid phase is also unknown, though it is possible to regard liquid crystals as constituting a second liquid; of solid modifications (polymorphic forms) there may be a large number. If a second such solid form exists, the number of possible equilibria is increased by seven, since it can exist alone or in contact with each of the other three forms or in contact with each of the three combinations of two forms; the existence of a third solid form will of course increase the number of possible systems still more largely. It does not follow however that all of these systems which may be conceived as algebraical possibilities shall be capable of experimental realization; sometimes such equilibria can be shown to be necessarily false, and in many other cases the experimental requirements of temperature or pressure cannot be met. Nevertheless, the number of such typical systems which have been studied is very large, indeed much too large for systematic treatment within the limits of this chapter; still less will it be possible to illustrate all possible types of equilibria for two-component or multi-component systems. A few examples of the better known one-component, two-component and three-component systems will be discussed, with whatever generalizations may be drawn from them; for more exhaustive study, the student is referred to any of the several treatises on the phase rule.[1]

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[1] It is worth noting that the actual *mass* of the phase plays no part in the equation, and hence has no influence upon the equilibrium. This is a fundamental feature of heterogeneous equilibria. It was recognized before the statement of the phase rule, and finds expression for example in the well-known tenet that in mass-law equilibria the "active mass" of the solid is constant.

[2] This statement is true only in a restricted sense. The amount of material per unit volume, or density, of course varies from phase to phase, and the density (or specific volume) may therefore be regarded as a third independent variable. The familiar diagram of the pressure-volume relations of the gaseous and liquid state, showing the equality of volumes at the critical point, is the commonest example in which the volume is treated as an independent variable.

Water: In proceeding to a study of this substance, it will be simplest if we recount the well-known facts with reference to its occurrence in different phases and then interpret them in terms of the phase rule. These outstanding facts are that the liquid has a vapor pressure which increases with the temperature (amounting to 760 mm. of mercury at 100°, which is its boiling point) until the temperature reaches 374° C., at which point it undergoes the critical phenomena; that, upon cooling, it freezes to form ice at 0° under atmospheric pressure, which solid also has a small but measurable vapor pressure; and, lastly, that this freezing point is lowered by increased pressure. The statement of these well-known facts implies the following phase equilibria: (1) liquid water and its vapor, in which the vapor pressure increases with the temperature, (2) ice and vapor, in which the vapor pressure and temperature bear a similar relationship, (3) solid and liquid, in which the melting point decreases with pressure increase, and (4) solid, liquid and vapor, existing together only at a fixed temperature of approximately 0° C. In these four equilibria, pressure and temperature are the only variables mentioned; in this system there can be no variations in composition, since each phase is wholly water under all conditions. The quantitative data for these relationships are given in the following table.

The same data are shown schematically in Fig. 4, in which the pressure is written as ordinate and the temperature as abscissa. Three curves result, representing the three univariant equilibria. The curve COt_c, which will be discussed first, represents the equilibrium between liquid water and vapor, and is the so-called *vapor pressure curve for water.* For every temperature there

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[1] Die heterogenen Gleichgewichte, Braunschweig; vol. 1 and 2, I by Roozeboom, 1901 and 1904; 2, II by Buchner, 1918, 2, III by Aten, 1918, 3, I and II by Schreinemakers, 1911 and 1913. The Phase Rule, by Bancroft, 1897. The Phase Rule and its Applications, Findlay, 1923 (5th edition). The Principles of the Phase Theory, Clibbens, 1920.

TABLE XII

EQUILIBRIUM PRESSURES FOR WATER

Temp. C.	Water + Vapor	Ice + Vapor	Ice + Water
	$L \rightleftharpoons V$	$S \rightleftharpoons V$	$S \rightleftharpoons L$
− 20		0.770 mm. of Hg	1970 kg. per sq. cm.
− 15		1.237 " " "	1590 " " " "
− 10	2.144 mm. of Hg	1.947 " " "	1130 " " " "
− 5			610 " " " "
0	4.579 " " "	4.579 " " "	1 atmosphere
+ 20	17.539 " " "		
+ 100	760.00 " " "		
+ 200	15.3 atmospheres		
+ 300	84.6 "		
+ 374	217.5 "		

exists one pressure, and only one, which can be exerted by the system, and for each pressure one temperature and only one at which equilibrium can be maintained, which is simply the more lengthy way of stating that the system consisting of liquid water and vapor is univariant, and that the selection of a temperature defines the pressure or the selection of a pressure defines the temperature. This will be recognized, also, as a restatement of the long-known fact that the vapor pressure of water depends only upon the temperature. If, however, at a given temperature, a pressure is maintained above that indicated on the line Ot_c, the vapor will be compressed wholly into the liquid phase; or if the pressure is maintained below the equilibrium pressure, the liquid will wholly evaporate.

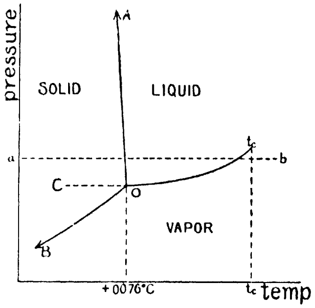

FIG. 4. p-t Diagram for Water (Schematic)

Our information about the vapor tension curve COt_c might be called complete if we were in position to state its origin, its terminus, and its position at all intermediate points. In the case of water, we have a large part of this information. Careful experimental measurements of the vapor pressure have been made by a large number of investigators, and may be found in the tables of physical constants. Were we not in possession of this material, however, we could at least determine qualitatively that the curve rises with the temperature by the application of the van't Hoff law of mobile equilibrium, which, with Le Chatelier's theorem, is the handiest tool in the application of the phase rule. The change of liquid into vapor is an endothermic change, and hence by application of the rule, the equilibrium will be moved in that direction by a rise in temperature. Further, the Clapeyron-Clausius thermodynamic equation

$$\frac{dp}{T} = \frac{\lambda}{T\Delta V},$$

in which λ is the heat of vaporization and ΔV the change of volume on vaporization, gives the slope of the curve.

The upper end of the vapor-pressure curve for water, or indeed for any liquid, is the critical point t_c, which has been discussed in an earlier chapter. Study of the two phases, water and vapor, shows that, as the temperature and pressure rise, the liquid becomes less dense and the vapor more dense, and the heat of vaporization becomes less and less; if the temperature rise be carried far enough, the two phases will become of the same density and the heat of the change will become zero; or, in other words, the two phases will become identical upon reaching this critical state. In general terms, the critical state is that state, approaching which coexistent phases approach identity, and at which they become identical. For water, the critical temperature is 374° and the critical pressure 217.5 atmospheres; it is an invariant point, since neither pressure nor temperature may be altered. As previously explained, the additional restriction that the two phases shall be identical puts the occurrence in accordance with the phase-rule equation. Above this temperature and pressure, water exists in a state for which no general name has as yet been adopted; the distinction between the liquid state and the gaseous state has vanished, and the areas V and L in Fig. 4 pass into each other without discontinuity.

Passing to the lower section of the vaporization curve COt_c, the point O represents the temperature at which water ordinarily freezes. With sufficient care however water may be cooled considerably below this temperature without the formation of ice, and from such experiments a prolongation OC of the vapor pressure curve has been drawn to represent the still perfectly definite relations of pressure to temperature. The extent of this prolongation is, however, indeterminate; the point C therefore represents no definite end to the curve. Throughout the whole course of the section OC the system water + vapor is metastable, in that it will, on contact with a nucleus of ice or sometimes without such contact, change into the system ice + vapor; the irreversibility of this change will appear a little later.

The curve OB in Fig. 4 represents the equilibrium curve for ice plus vapor, and is spoken of as the vapor pressure curve of ice or sometimes as its sublimation curve. Its lower end B is assumed to be at the absolute zero of temperature and the application of van't Hoff's law would again indicate pressure increase with increase of temperature The experimental figures for this curve, some of which are given in column 3 of Table XII, place the curve below that for water + vapor (OC) throughout its course, but its steeper curvature brings about an intersection of the two at a temperature very close to 0°. The positions of the two curves OB and OC may be used to explain the stability relationships of the two systems. If, at some constant temperature below that of the point O, ice is set in one vessel and water in a second under a bell-jar, the vapor pressure of the system water + vapor will be greater than that of the other, and as a result vapor passing from the liquid will solidify upon the ice until the liquid has entirely disappeared. In such a case it is obvious that the unstable system is the system with the higher vapor pressure.

The intersection of the two curves at the point O represents a new equilibrium. Ice and vapor are in equilibrium, water and vapor are in equilibrium, and the vapor is the same in pressure in both cases; it follows then that ice and water must also be in equilibrium, and the curve representing that equilibrium (OA) must pass through the point O, which is therefore the intersection of three curves. Roozeboom first suggested that such a point be called a "triple point." It represents an invariant condition, in which neither pressure nor temperature can be changed without the elimination of a phase. The temperature and pressure corresponding to this triple point have been carefully determined; the pressure is 4.579 mm. of mercury and the temperature + 0.0075°. (The occasion of this variation from the commonly accepted freezing point of 0° will be explained a little later.) At this temperature and pressure, and only here, can a system consisting of water be maintained in the three coexisting states of ice, liquid and vapor.

The triple point *O* has been shown to be the origin of the curve *OA*, representing the equilibrium between ice and liquid in the absence of vapor. It has long been known[1] that the melting point of ice, that is, the equilibrium temperature, is altered by pressure. Whether an increase of pressure will raise or lower the melting point may be easily deduced from Le Chatelier's theorem; increased pressure will shift the equilibrium in the direction which reduces the pressure within the system, which is in the direction producing smaller volume, and since, in the case of water, the liquid has a smaller volume than the solid (i.e., is denser), increased pressure at constant temperature results in liquefying ice. The curve *OA* is therefore inclined upward toward the pressure axis, so that at any temperature represented upon it an increased pressure (measured upward) brings the system into the region of liquid alone; or, otherwise stated, the freezing point is lowered by increased pressure. The curve is not a straight line, but is slightly concave toward the pressure axis; a few of the corresponding pressures and melting points are given in Table XII, column 4.

Before considering the extension of the curve *OA* toward very high pressures, it will be well to compare Fig. 4 with our common knowledge of the behavior of water, upon which we have built our discussion In one particular, the figure differs from our usual laboratory experience, in laboratory practice the freezing point of water is taken as exactly 0°, whereas in our discussion we have stated it to be + 0.0075° Line 5 of Table XII shows for 0° a lack of agreement in the pressures of the three monovariant equilibria. We have here, however, no contradictions to the phase rule to explain, nor even inexact data to excuse; the explanation is that our data and our discussion are applicable to systems consisting of water alone, in which the pressure is that caused by water vapor, while our laboratory practice is carried out in open vessels in which a second component is present, namely, air, and in which a constant pressure of one atmosphere is exerted. Since a second component is present, a system consisting of ice, water, and the gas phase is *not* invariant, as may be seen by substitution in the phase-rule equation, but is univariant, and there can be any number of temperatures at which the system can exist with corresponding pressures. Actually, however, the effect of the air as an added component is not great, since it is probably not present at all in the solid phase and its solubility in the liquid is not large More important, however, is the fact that its presence puts the system under a pressure of one atmosphere instead of the small vapor pressure of water, and in accordance with the reasoning already used the melting point of the ice is depressed from + 0.0075° to 0° The vapor pressures are of course also affected slightly by the change in temperature and composition, but the difference is very small. To state the facts as succinctly as possible, + 0.0075° is the triple point for the one-component invariant system, ice, water and vapor, and the corresponding vapor pressure is 4.579 mm., 0° is the equilibrium temperature in the two-component system consisting of water and air, where the phases are ice, aqueous solution of air and vapor phase and the total pressure is one atmosphere.[2]

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[1] James and William Thomson, *Trans. Roy. Soc. Edin.*, **16**, 575 (1849); *Proc. Roy. Soc. Edin.*, **2**, 267 (1850).

[2] More strictly speaking, water and air make up a multi-component system, since the air does not dissolve as such in the liquid, but gives to the water concentrations of oxygen.

The freezing point of water is one of our best known fixed points and is a standard temperature used in the marking of thermometers. While not independent of the pressure, it varies so slightly that fluctuations of barometric pressure such as occur with changes of weather are negligibly small. Any triple point in a one-component system, or more commonly any one-component solid-liquid-vapor complex in the presence of air at 1 atmosphere pressure, is in principle suitable for the standardization of thermometers; in practice certain invariant systems of two components (air not being considered) are found more convenient, consisting of a salt and water and giving rise to very accurately determined eutectics and transition points of a hydrate to a lower hydrate or to the anhydrous form; examples will be given later.

Returning to the fusion curve OA, it has been found that at high pressures there exist several polymorphic forms of ice, differing from the common variety in density, heat of formation, crystalline structure and other physical properties. Tammann[1] was the first to discover that, at sufficiently high pressures, new modifications of ice appear, and his work together with that of Bridgman[2] gives a fairly complete picture of the phase relations which exist. There are at least five polymorphic forms of ice, known as ice I (the common form), ice II, ice III, ice V, and ice VI, the positions of which in the $p-t$ diagram are shown in Fig. 5. The relationships of ice IV are not clearly known, and it is not included in the sketch. Each of these five forms has definite limitations of pressure and temperature within which it can exist as a stable form, at the

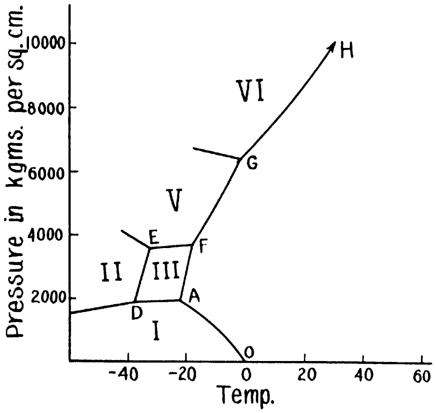

FIG 5. p.-t. Diagram for Water at High Pressures

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nitrogen, argon, carbon dioxide, etc., depending upon their solubility and their partial pressure. Since the principal effect of the air is due to its pressure rather than to the components which it adds, this further complexity may be neglected.

[1] *Ann. Physik.*, (4) **2**, 1 and 424 (1900); *Z. physik. Chem.*, **72**, 609 (1910); **84**, 257 (1913); **88**, 57 (1914).

[2] *Z. anorg. Chem.*, **77**, 377 (1912); *Proc. Nat. Acad. Sci.*, **47**, 441 (1912); *Z. physik. Chem.*, **86**, 513 (1914).

boundaries of which it can exist in stable equilibrium with other forms and outside of which it can have only metastable existence. These boundary curves represent univariant equilibria, in the same sense as the curves studied in Fig. 4; the experimental data for these curves will not be given here, but may be estimated approximately from the figure. Wherever three such boundary curves meet there exists a triple point, at which three phases coexist at the invariant temperature and pressure indicated. These triple points are of course all at pressures at which the vapor phase cannot exist, and consist of various combinations of two solid phases with the liquid and of three solids with each other. The entire list of such invariant equilibria is given in Table XIII in the order of increasing pressures, including the triple point for ice water and vapor previously discussed.

TABLE XIII

TRIPLE POINTS IN THE ONE-COMPONENT SYSTEM WATER

Position in Fig. 5	System	Type	Temperature	Pressure in Kgms. per Sq. Cm.
O	Ice I—liquid-vapor	$S_1 - L - V$	+ 0.0075	(4.579 mm.)
A	Ice I—ice III—liquid	$S_1 - S_2 - L$	− 22.0°	2115
D	Ice I—ice II—ice III	$S_1 - S_2 - S_3$	− 34.7°	2170
E	Ice II—ice III—ice V	$S_2 - S_3 - S_5$	− 24.3°	3510
F	Ice III—ice V—liquid	$S_3 - S_5 - L$	− 17.0°	3530
G	Ice V—ice VI—liquid	$S_5 - S_6 - L$	+ 0.16	6380

Of the various univariant equilibria, we will select for qualitative study those in which liquid and a solid are the coexisting phases, indicated by the curves *OA*, *AF*, *FG*, and *GH*. The curve *OA* has already been discussed, and its inclination toward the pressure axis shown to be in accord with Le Chatelier's theorem. The freezing point is depressed as the pressure is raised until a minimum temperature of − 22° is reached at a pressure of 2115 atmospheres. The temperature can now no longer be lowered, whatever the pressure, without causing the liquid to solidify completely; we may therefore consider − 22° as the minimum freezing point of water under any set of equilibrium conditions. If we now raise the pressure, a transition of ice I into ice III occurs, and unlike the transition occurring at *O*, it is marked by a decrease in volume; moreover, the new phase, ice III, is denser than water instead of less dense. If we now apply Le Chatelier's theorem, we will deduce that an increase of pressure will raise the freezing point, so that the equilibrium curve for ice III and water must slope upward away from the pressure axis, as shown by the line *AF*. Equilibrium temperatures therefore rise with the pressure until at *F* a new triple point is met and ice III is transformed into ice V by increase of pressure; the new equilibrium curve *FG* has a still more marked slope toward the right until it reaches the triple point *G*, at 6380 kgm. pressure and a temperature of + 0.16°. At this high pressure the freezing point of water (forming ice V or ice VI, of course, and not ice I) is very close to its freezing point at 1 atmosphere pressure. The equilibrium curve GH now inclines still more sharply toward the right, and has been investigated by Bridgman up to pressures of 20,000 kgm., at which the freezing point of water is + 80°. Of the four equilibrium curves for solid and liquid, but one (OA) slopes toward the pressure axis, because the specific volume of ice I is greater than that of liquid water; the other three incline away from the pressure axis, because ice III, ice V, and ice VI have each a specific volume less than that of water.

With this much of specific discussion of the application of the phase rule to water, we may see whether some of the relationships learned may not be given a more generalized treatment. The simple diagram (Fig. 4) may now be looked upon as a diagram for any system of one component in the neighborhood of the triple point for solid, liquid and vapor; the only differences for any system will be in the numerical values of the ordinates and abscissæ, and in the slopes of the three curves. The vapor pressure curve Ot_c will always rise with the temperature, though its slope may be greater or less than that for water, and will extend from the triple point up to the critical temperature and pressure, t_c; it will have a metastable prolongation OC which may be either short or long, depending upon the character of the liquid, more particularly upon its viscosity. The so-called amorphous condition of substances is regarded simply as the undercooled liquid in equilibrium with its vapor, as indicated by this metastable prolongation. Such amorphous bodies may show a most astonishing persistence in the metastable condition, even in the presence of the stable form; it is believed that, sufficiently far below the triple point, the rate of transformation becomes very slow because of the viscosity of the liquid and more particularly because of the diminishing number of nuclei from which the crystallization might spread. The vapor pressure curve for the solid, BO, will also rise with the temperature in all cases, the rate depending upon the nature of the particular substance. It will lie below the metastable curve OC, and will terminate at the triple point O, since metastable existence of a solid above its melting point in a one-component system has never been observed. The curve may have one or more transition points upon it at which it changes its direction discontinuously, if the solid exists in several polymorphic forms, just as in the curve $OAFGH$ in Fig. 5; a discussion of polymorphism is reserved for a later point in the chapter. The fusion curve OA and its continuation may slope upward either toward or away from the pressure axis according as the solid phase is less dense or more dense than the liquid, and may change its direction at any point, depending upon this relationship. Metastable prolongations of the curve below O are unknown. The question as to the further end of the fusion curve is a matter of conjecture. Ostwald believes that it ends in a critical point for the solid-liquid phases, at which the two have the same density and a zero heat of fusion. Roozeboom and Tammann incline to a belief in a much less simple hypothesis, according to which the fusion curve eventually inclines toward the pressure axis and describes more or less completely a closed circle, above which the area for the liquid phase is continuous. Experimental data are not complete enough to give any certainty as to the complete curve.

Treating the diagram of Fig. 4 as a general case, it is instructive to deduce the effect of changes of pressure or of temperature such as can usually be accomplished with little experimental difficulty. Let us consider the changes which will occur if such a system is taken at a temperature below the triple point and a pressure above it, as represented by the point a in the diagram, and then subjected to continuous addition of heat while the pressure is maintained constant; the results can all be deduced by following the phase changes along a line of equal pressure, ab, called an isobar. At a the system consists of solid alone, and addition of heat will bring about no changes except a rise of temperature and an increase of volume until the system reaches a condition represented by the intersection of *ab* with *OA*; here the solid begins to melt, and the temperature remains constant until the solid has completely liquefied. The liquid now rises in temperature again up to the point of intersection of the line *ab* with Ot_c, at which point it begins to vaporize and maintains a constant temperature until the liquid has completely changed to vapor. This evaporation of a liquid at a vapor pressure equal to the total pressure exerted upon the system is the ordinary process of boiling, and the intersection of the line *ab* with Ot_c is the boiling point; since *ab* is drawn at any arbitrary height, it follows that the boiling point is always arbitrarily determined by the pressure under which the system is standing. In ordinary laboratory practice our procedure differs from that sketched above only in that air is usually present either at atmospheric pressure or at a reduced pressure so that vapor of the liquid will be present in the vapor phase within the areas marked *S* and *L* in the diagram. If now the experiment be repeated with *ab* taken at some pressure below the triple point *O*, the changes are fewer; where the intersection with *BO* occurs, the solid vaporizes completely without change of temperature and the process is spoken of as sublimation. If for example the substance taken be solid carbon dioxide and the pressure 1 atmosphere, our second case is exactly described, for the triple point *O* is at a pressure of 5.1 atmospheres and a temperature of − 56.7°[1]; the isobar *ab* drawn at 1 atmosphere pressure intersects the curve *BO* at − 78.3°, at which temperature the solid will remain until sublimation is complete, giving a very simple and convenient method of securing a constant low temperature. Ice, in order to be sublimed without melting, must be maintained under a pressure lower than 4.6 mm., the pressure at its triple point; and iodine, which melts at 114° and a pressure of 91 mm., must be maintained below that temperature and pressure if melting is to be excluded. In the latter case, for laboratory sublimation the process is usually to maintain a constant temperature of 100° at atmospheric pressure, allowing the vapor to diffuse outward until it meets some cool surface upon which it solidifies; this is a process of evaporation rather than sublimation, in that the constant temperature is maintained by the environment whereas in true sublimation the environment is at a higher temperature and the constant and lower temperature of the system is fixed by the pressure and maintained by means of the negative heat of vaporization.

The result of changing the pressure at constant temperature can be deduced by following a line drawn parallel to the pressure axis, and called an isotherm, or isothermal line. If, for a system represented by Fig. 4, the isotherm be drawn at a temperature just below the point *O*, the system will be wholly gaseous at low pressures; as the pressure is raised its volume will diminish until when the intersection with the line *BO* is reached the vapor completely solidifies without increase of pressure; when the intersection with the curve *OA* is reached, the solid will melt completely without increase of pressure. If the isotherm is drawn above the point O, a single change from vapor to liquid will occur at the pressure of the intersection with Ot_t.

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[1] Thiel and Caspar, *Z. physik. Chem.*, **86**, 257 (1914).

Sulfur: Sulfur is commonly known in two crystalline modifications, rhombic sulfur and monoclinic sulfur; these have a transition temperature (96°) at which they are in equilibrium with each other. Each possesses a melting point, that of the rhombic being approximately 114° and that of the monoclinic about 120°. The liquid form of sulfur undergoes some rather remarkable changes in color and viscosity when heated, and boils at 444.7° C. On rapid cooling of very hot molten sulfur a brownish gum is obtained, called plastic sulfur, which slowly changes into a hard brittle substance, while if sulfur only slightly above its melting point is quickly cooled, the yellow substance is at once formed; these two quickly cooled products differ considerably in their solubility in carbon disulfide, the latter being much the more soluble; they contain varying amounts of a quasi-solid called amorphous sulfur. These are the commonest facts about the substance, which we shall proceed to relate in accordance with the phase rule, although it is only fair to state that by no means all the relationships are known or classified.

These relationships are shown qualitatively in Fig. 6. The right-hand part of the diagram (curves OB, BE and BC) will be recognized as nearly duplicating the diagram for water; OB is the sublimation curve for monoclinic sulfur (univariant equilibrium $S_M \rightleftarrows V$), BE is the vapor pressure curve for liquid sulfur (univariant equilibrium $L \rightleftarrows V$), and their intersection at B is the triple point for the invariant equilibrium $S_M - L - V$, the temperature being 120°. BC is the fusion curve for monoclinic sulfur; since the solid form is denser than the liquid, as is the case in the majority of instances, the curve slopes upward away from the pressure axis. At C there is a second triple point, at which rhombic sulfur, monoclinic sulfur and liquid are in equilibrium; the temperature is 151° and the pressure 1320 kgm. per sq. cm.[1]; the curve CD is the fusion curve for rhombic sulfur. For relationships not met with in the study of water we look to the left of the diagram, where we find the curve AO indicating the vapor pressure of rhombic sulfur. The point O is the transition temperature of the two solid forms, 96°, and is a triple point at which the two solids and vapor are in invariant equilibrium; it is also the point of intersection of the curve

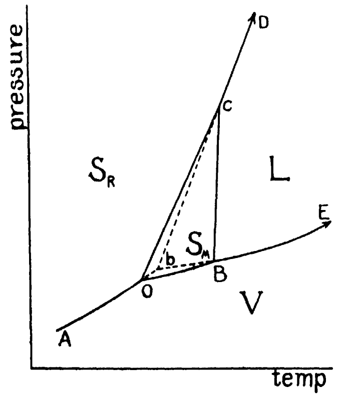

FIG. 6. p.-t. Diagram for Sulfur (Schematic)

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[1] Tammann, *Wied. Ann.*, **68**, 675 (1899); *Ann. Physik.*, **3**, 178 (1900).

OC, which is the transition curve of the two solids. Since the two solids alone make up a univariant system, it follows that the transition temperature must vary with the pressure. Arguing backward from the diagram to the facts, it may be deduced from the slope of *OC*, by Le Chatelier's theorem, that rhombic sulfur is more dense than monoclinic; the densities are 2.04 and 1.93. The greater slope of the curve *OC* brings about its intersection with *BC* at the triple point *C* already mentioned. This series of curves, if drawn to accord with the experimental data, makes a division of the entire pressure-temperature diagram into four areas, one each for the vapor, liquid sulfur, rhombic sulfur and monoclinic sulfur; the area for the stable existence of monoclinic sulfur, *OBC*, is completely enclosed by the other three.

In addition to the stable equilibria discussed above, there are several metastable equilibria indicated by the dotted lines of Fig. 6. With the metastable vapor-pressure curve of the liquid, *Bb*, we are already familiar from our study of water. In the metastable curve *Ob*, the prolongation of *AO*, is represented the possibility of heating a solid above its transition point into a second solid; this phenomenon is extremely common, and is unquestionably connected with the fact that the rigidity of solids retards the molecular rearrangements necessary for a change in crystalline form. The intersection *b* will be recognized as the metastable melting point of rhombic sulfur, found to be at about 114°, but doubtless with some error, as will appear later. From this melting point, which is of course a triple point, the metastable fusion curve (*bC*) of rhombic sulfur into liquid runs upward to *C*, above which it is continued as the stable fusion curve *CD* mentioned earlier.

The equilibria indicated in the diagram are seen to be numerous. There are four bivariant equilibria, represented in the diagram by areas within which a single phase can exist and within which *both* the temperature and the pressure may be varied, there are six univariant equilibria, represented by lines, indicating two coexisting phases, which may have *either* temperature or pressure varied at will, but not both, and finally there are four invariant equilibria (one being metastable), represented by the points of intersection and indicating that the three coexisting phases can have neither temperature nor pressure altered. The list of univariant and invariant equilibria follows

TABLE XIV

EQUILIBRIA OF SULFUR

Univariant Equilibria		Invariant Equilibria			
Line	Phases Present	Point	Phases	Temp.	Pressure
AO (*Ob*)	$S_R—V$	*O*	$S_R—S_M—V$	96°	
OB	$S_M—V$	*B*	$S_M—L—V$	120°	
EB (*Bb*)	$L—V$	*C*	$S_R—S_M—L$	151°	1320 kgm.
BC	$S_M—L$	*b* (metastable)	$S_R—L—V$	114°	
OC	$S_R—S_M$				
DC (*Cb*)	$S_R—L$				

Passing to a consideration of liquid sulfur, its peculiar properties have been studied and explained chiefly by Alexander Smith[1] and his coworkers, who have established that in the liquid state, as also in the vapor state, sulfur consists of two forms in dynamic equilibrium; to these Smith gave the names sulfur lambda (S_λ) and sulfur mu (S_μ). These differ in their molecular weight, S_λ being of the formula S_8 and S_μ having a lower molecular weight, probably corresponding to S_4. Such dynamic equilibria of liquid or gaseous substances are of course well known; we meet instances in the various cases of tautomerism, and even as simple a substance as water in the liquid state consists of various isomers such as monohydrol (H_2O), dihydrol $(H_2O)_2$, etc., in equilibrium. The peculiarities of the sulfur equilibrium however, to which we may ascribe most of the behavior in which it differs from other substances, are two in number: first, the unusual character of the equilibrium curve, and secondly the relative slowness with which the equilibrium $S_\lambda \rightleftharpoons S_\mu$ is established, making it possible to maintain and study the system in metastable equilibrium by sudden drop in temperature or by use of negative catalysts (SO_2 being very effective) as well as to study true equilibrium mixtures, using positive catalysts such as ammonia, if necessary, to accelerate the attainment of equilibrium. The figures for the composition of liquid sulfur, as obtained by Smith, are as follows; later work by others has given data differing from Smith's by a few per cent only.[2]

TABLE XV

DYNAMIC EQUILIBRIUM: S_λ AND S_μ

Temperature ° C.	130	140	150	160	170	180	200	220	240	310	448
% S_μ	4.2	5.6	6.7	11.0	18.7	22.5	27.0	29.4	33.0	32.6	34.1
% S_λ	95.8	94.4	93.3	89.0	81.3	77.5	73.0	70.6	67.0	67.4	65.9

When these data are plotted (Fig. 7), it appears that the most rapid changes in composition of the liquid occur between 150° and 200°, and if more narrowly scrutinized, between 160° and 170°. Now, if we consider the contrast in the properties of pure S_λ and S_μ, we shall be in position to understand the striking changes which the liquid solution undergoes at about 160° to 170°. S_λ is light yellow in color, of small viscosity and soluble in carbon disulfide, while S_μ is dark brown in color, quite viscous, and insoluble in that solvent. Liquid sulfur at lower temperatures, consisting largely of S_λ, will therefore have a color and viscosity nearly that of that pure substance; if heated to 160°–170° or above, the considerable increase in the proportion of S_μ gives the liquid its well-known dark color and high viscosity. Let us now assume a mass of molten sulfur at some high temperature, where it contains some thirty per cent of S_μ to be suddenly cooled by pouring into cold water; the proportions are but slightly altered by the change, in accordance with the observed fact that the speed of the reaction is low, and the plastic sulfur thus obtained is a brown viscous gum, which is to be regarded simply as the undercooled solution of the two forms. If it is treated with carbon disulfide, the soluble S_λ is extracted and the residue is undercooled S_μ; it is considered to be the amorphous form of sulfur. Being metastable at these low temperatures, it will in time change into the stable form, which is rhombic sulfur, as shown in Fig. 6. If the liquid chosen for cooling be taken at a temperature below 160°, the proportion of insoluble sulfur present is small, and the material obtained by chilling is chiefly soluble crystalline sulfur. On a theory that the solid phases are not composed of a single form, but are, like the liquid, equilibrium solutions (that is, solid solutions), Smits[1] has suggested a diagram into which all the forms can be fitted.

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[1] Smith and others, *J. Am. Chem. Soc.*, **27**, 801, 983 (1905); *Z. physik. Chem.*, **42**, 469 (1903); **52**, 602 (1905); **54**, 257 (1906); **57**, 685 (1907); **61**, 200 (1907); **77**, 661 (1911).

[2] For brevity's sake no reference is made here to the existence of the third dynamic isomer, S_π, whose existence has been shown by Aten and confirmed by Beckmann et al. (*Z. anorg. Chem.*, **103**, 189 (1918)). For a bibliography of the work on sulfur up to 1918, see vol. 2, part III of Roozeboom's Die heterogenen Gleichgewichte, issued by Aten in 1918.

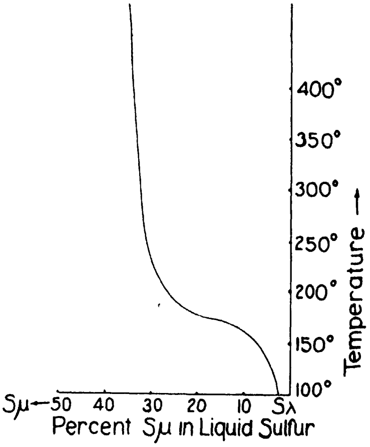

FIG. 7. Equilibrium $S_\lambda \rightleftharpoons S_\mu$ in Liquid Sulfur

The fact of the slow establishment of equilibrium in the liquid phase leads to some important considerations relative to the melting point of sulfur. A melting point is the temperature of equilibrium between the solid phase and the liquid phase, under the pressure of the system. Disregarding the matter of the small effect of substituting atmospheric pressure for the pressure of the system, it is clear that as many as three equilibria may be involved: (1) equilibrium *within* the liquid phase, if it is capable of existing in two or more forms between which changes can occur, (2) equilibrium *between* the liquid phase and the solid phase, and (3) equilibrium *within* the solid phase, if solid solution of two or more forms exists. It is logically a necessity that, while only one equilibrium temperature is possible when all three equilibria have been attained, an indefinite number of temperatures is possible if any one or two of the equilibria have not been reached. Leaving out of consideration, for simplicity, the possibility of metastable conditions in the solid phase, we see that possibilities of complications in the liquid phase may frequently occur. In our study of water it was unnecessary to consider this point, inasmuch as the dynamic equilibrium between monohydrol, dihydrol, etc., is attained instantaneously in the liquid state; liquid water is therefore always in the same condition at a given temperature, and more than a single freezing point (pressure being assumed constant) is not found. But, in the case of liquid sulfur, the liquid phase may have present, according to its history, proportions of S_λ and S_μ widely different from the true equilibrium quantities, because of the slowness with which equilibrium is reached, and the equilibrium temperature with the solid phase, or melting point, may vary from that of pure S_λ in contact with solid to that of a solution containing a large proportion of S_μ. The melting points thus obtained are plotted in Fig. 8. The line *AC* represents the melting point curve for monoclinic sulfur and *DF* that for rhombic. On these curves there are four points of especial interest; these are the two melting points in contact with pure S_λ and S_μ, which have been called the ideal melting points (*A* and *D*), and the two melting points in contact with the true equilibrium proportions of S_λ and S_μ in the liquid phase (*B* and *E*), appropriately named the natural melting points. The curve *BE* is the curve for the dynamic equilibrium in the liquid phase. In Table XVI are given the figures for these melting points as determined by Smith and Carson.[1] It will be observed that these temperatures are sensibly different from those commonly given for the two forms, the discrepancy being greatest in the case of rhombic sulfur.

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[1] *Z. physik. Chem.*, **83**, 221 (1913), also Die Theorie der Allotropie (Barth, 1921). English Translation by Thomas, Longmans, Green and Co., 1923.

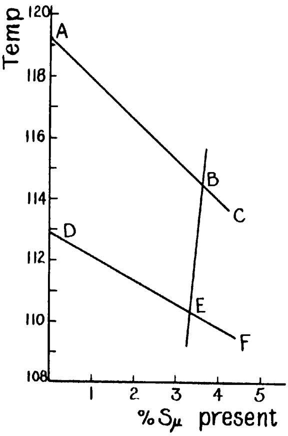

FIG. 8. Melting Point Curves of Monoclinic and Rhombic Sulfur

TABLE XVI

MELTING POINTS OF RHOMBIC AND MONOCLINIC SULFUR

	Ideal Melting Points	Natural Melting Points	S_μ at Natural M P.
Monoclinic Sulfur	119.25°	114.5°	3 6 %
Rhombic Sulfur . .	112.8°	110.2°	3.4 %

A consideration of the above set of facts, depending upon a slow attainment of dynamic equilibrium in the liquid phase, leads to an interesting deduction relative to the number of components of the system. Let it be supposed that in a case of dynamic equilibrium the equilibrium is reached with infinite slowness, that is, that any solution remains perfectly stable and unchanged in its composition; it will follow then that the system is a two-component system, since it will be impossible to express the composition of the liquid in terms of any one substance. Such a system will then have the degree of freedom, or variance, corresponding to a two-component system, that is, one degree of variance higher than if calculated for a one-component system with the same number of phases present; for example, with vapor, solid and liquid present the equilibrium temperature (melting point) is not invariant, but is univariant, varying with the composition. Such would be the case in a system consisting of two isomeric compounds, such for example as ortho-cresol and para-cresol. Now, we have, as a matter of fact, just seen that the melting points of sulfur show just this relation, and we have been treating the system essentially as a two-component system in our latter discussion. A distinction exists here however in that, within reasonable time, equilibrium within the phase is reached, and *once that condition has been attained* the system can be treated as of one component without error, it is therefore spoken of as a pseudo-binary system, since it has, under certain conditions, the properties of a two-component or binary system. It is evident that the distinction between a one-component system (unary system) like water, a two-component system (binary system) like the two cresols, and a pseudo-binary system like sulfur depends upon the speed with which equilibrium is attained within a phase.

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[1] *Z. physik. Chem.*, **77**, 670 (1911).

In concluding the direct study of sulfur, it should be stated that reference has been omitted to a fourth dynamic isomeride, S_ρ, and to two other metastable solids, S_{III} (nacreous sulfur) and S_{IV}, for the treatment of which the reader is referred to the monographs on the phase rule and the original literature in the journals.

GENERAL CONSIDERATIONS RELATIVE TO ONE-COMPONENT SYSTEMS

Polymorphism: In the discussion of water reference was made to the several solid modifications which have lately been discovered; and in the discussion of sulfur the rhombic and monoclinic forms were considered. These are individual instances of the general phenomenon known as *polymorphism.*

Polymorphic forms are solid phases of the same ultimate composition, differing among themselves in crystalline form, free energy and other physical and chemical properties, but yielding identical liquid or gaseous phases upon fusion or evaporation. In cases where the polymorphic forms are composed of a single element (sulfur, phosphorus, carbon, tin, etc.), it is usual to speak of the forms as allotropic, while if the forms are of compound composition, as is the case with ammonium nitrate, silver nitrate, mercuric iodide, etc., the general class name is used, allotropism is therefore simply a special case of polymorphism. Every polymorphic form exists as a separate phase, and the number of solid phases for a single component is therefore the number of polymorphic forms existent. By the application of the definition given we can clearly differentiate polymorphism from isomerism, in the latter case, we have differing solid modifications of the same composition which however continue to maintain their differences in the liquid or gaseous state, and any system made of isomers is therefore a two-component or multi-component system, since the phases cannot have their composition expressed by less than two terms.

With the question as to the ultimate condition in polymorphic solids the phase rule is not concerned; the difference may lie in the geometrical arrangement of the molecular units making up the crystals, in the molecular weight, or possibly in the proportions of different molecular species existing in dynamic equilibrium.[1] It is the interrelationships of these forms, as separate phases, that the phase rule is in position to classify. In many cases, of which sulfur is one, it has been found that two polymorphic forms possess vapor tension curves which approach each other with alterations in the temperature, intersecting at a point (called the *transition point*) at which the vapor pressures are identical. At such a transition temperature, and only there, are both solid phases stable; here an equilibrium exists between them such that addition of heat will effect a transformation into the form stable at higher temperatures, without however raising the temperature until the other form has disappeared, since the change is at an invariant point (triple point). Abstraction of heat brings about the reverse change, also at constant temperature. Polymorphic forms, which stand in the relation of possessing such a transition point at which they are in equilibrium, are known as *enantiotropic forms;* enantiotropy has been illustrated in the study of water and of sulfur and is frequently met with. Tin offers an interesting example of this sort, possessing a transition temperature of 18°, above which the stable form is white and has a density of 7.24, and below which the stable form is gray and has a density of 5.8. Not only many metals, but many compounds, such as ammonium nitrate, silver nitrate and mercuric iodide, exist in enantiotropic forms.

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[1] For discussion, see Smits, Die Theorie der Allotropie (Barth, 1921), translated by Smeath Thomas (Longmans, Green and Co.).

In other instances of polymorphism, the vapor pressure curves of the two forms do not meet; such forms, which lack a transition point, are called *monotropic*. It follows that under all conditions where both can exist, the one form is always stable, and the other is always metastable. The metastable form always has the higher vapor pressure, and will therefore change into the stable form by a process of distillation such as was illustrated in the case of undercooled water and ice; the rate of such a change may however be almost infinitely slow, especially where the actual vapor pressures are very small. An example of monotropism is found in the case of phosphorus; white (or waxy) phosphorus is metastable with respect to red phosphorus and possesses a higher vapor pressure at all temperatures up to its melting point, 44.1°; at room temperature, however, its rate of change into red phosphorus is extremely slow, so that the common method of preparing the red variety from the yellow consists in using high temperatures such as 250-300°, at which equilibrium is much more quickly obtained, and the vapor formed from the liquid yellow variety may condense as red phosphorus. In other cases it is not easy to determine whether a given form is monotropic or enantiotropic; thus, in the case of carbon, graphite is known to be the stable form at very high temperatures and diamond the unstable, but decisive experiments have not been performed to determine whether or not there is a transition point at some temperature below 1000°. Whichever is the stable form at low temperatures, the rate of transformation is infinitely slow, which is by no means incredible at temperatures so far below the melting point. If there is a transition point not yet found, the two forms of carbon would then be considered as pseudomonotropic rather than truly monotropic.

With this added knowledge as to polymorphic solid forms, a brief re-inspection of Figs. 4, 5, and 6 will lead to a simple but useful generalization. It will be observed that the equilibrium curve for any phases indicated is always continuous; discontinuity in direction occurs only where two or more curves intersect, that is, where an increase in the number of phases occurs. The newly appearing phase may be vapor, liquid, or any solid polymorphic form. In experimental work the appearance of a discontinuity in any type of equilibrium curve is a sure sign of a change of phase, and demands search for and identification of the new phase; the rule applies not only for one-component systems, but equally for those of more than a single component.

Condensed Systems: In the case of equilibria between solid phases and liquid phases (solubility, freezing points, etc.), the effects of moderate changes in pressure are very small, and in many cases may be ignored. Thus, the freezing point of water under its own pressure and under one atmosphere pressure differ by only 0.0075°, an amount which is not of significance in most measurements.

Such systems, consisting of solid and liquid phases only, are called *condensed systems*, and we may therefore treat condensed systems as independent of the pressure within moderate limits. This is a matter of much convenience in experimental work. In treating a condensed system, therefore, we may work either under some constant pressure, sufficiently high to prevent the formation of a vapor phase, or, as is more commonly done, work with open vessels under the atmospheric pressure, ignoring the fact that the pressure is not the true equilibrium pressure of the system and likewise ignoring the presence of the air as an additional phase, as has been discussed with respect to the triple point for water, the error involved by so doing is usually less than the experimental error in determining the temperature or in measuring the solubility.

Liquid Crystals:

Beginning with a discovery by Reinitzer[1] in 1888, a number of organic compounds have been observed to undergo changes upon heating which cannot be reconciled with the theory that pure substances exist only as vapors, liquids, and polymorphic solids. When solid cholesteryl acetate, which Reinitzer investigated, is heated, it apparently melts sharply at a given temperature, giving rise to a substance that possesses the most obvious properties of a liquid, that is, it possesses fluidity, and will form droplets if suspended in another liquid of equal density. On the other hand, it possesses certain properties hitherto only observed in solids, it is turbid or milky in appearance, and (most important of all) is *anisotropic*, showing double refraction and giving interference colors on examination by polarized light. At a higher temperature a second transition point is reached, at which the peculiar substance changes to a liquid of entirely normal character

The effort to explain such substances as emulsions or similar heterogeneous systems has not been successful, and they have been accepted as constituting a new type of phase and are called liquid crystals. Their classification as "crystals" is justified because of their showing properties which depend upon a regularly orientated internal condition; such are the anisotropic behavior referred to above, the existence of a space-lattice structure as shown by X-ray analysis[2] in the case of *p*-azoxyanisole, and the possession of a perfectly definite transition point (or melting point) into normal liquids, which melting point is affected by pressure or the presence of a second component in the same fashion as the melting point of unquestioned solids.[3] The belief that the liquid crystals are heterogeneous could not be maintained after it was shown that the turbidity is only apparent, being due to diffraction caused by differently oriented crystals and vanishing upon examination of the smaller units in the field of the microscope, indeed, liquid crystals have been prepared[4] which fail to show any turbidity when examined by unaided vision.

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[1] *Monats.*, **9**, 435 (1885).

[2] Lingen, *J. Franklin Inst.*, **191**, 651 (1921), **192**, 511 (1921).

[3] For a bibliography of the extensive researches on liquid crystals, see Findlay's Phase Rule, 5th Edition (1923), p. 41.

[4] Vörlander and Kasten, *Ber.*, **41**, 2033 (1908).

Viewing the liquid crystals as an independent type of phase, they may be fitted into the phase-rule diagram as shown in Fig. 9. The point *O* represents the triple point for solid, liquid crystals and vapor, and is called simply a transition point without any new specific name; the point *B* is the triple point liquid crystal + liquid + vapor, and is named the melting point, being entirely analogous to the melting point as usually defined. In Table XVII are given the data for several illustrations. It should be stated however that the study of liquid crystals is not yet complete enough so that a perfectly general treatment can be made which will fit the liquid crystals as a stable or metastable phase into all one-component systems, as can be done with the solid, liquid and vapor phases.

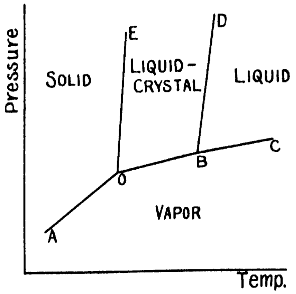

Fig. 9. One Component System including Liquid-Crystal Phase

TABLE XVII

Triple Points for Liquid Crystals

Substance	Transition Point *O*	Melting Point *B*
Cholesteryl benzoate	145.5°	178.5°
p-Azoxyanisol	118.3°	135.9°
p-Azoxyphenetol	134.5°	168.1°
Condensation product: benzaldehyde + benzidine	234°	260°
Azine of p-oxyethylbenzaldehyde	172	196
Condensation product: p-tolylaldehyde + benzidine	231	—
p-Methoxy cinnamic acid	169°	185°

Suspended Transformation: Suspended transformation has been referred to in the instance of the undercooling of liquid water, as represented in Fig. 4 by the curve *OC*, and in the case of sulfur (Fig. 6) suspended transformation is indicated by the curves *Ob* and *Bb*. In general, where a series of coexisting phases can be maintained in metastable equilibrium, that is, under conditions where complete representation of the system shows that a different combination of phases, pressures and temperatures is the stable arrangement, the system is said to show suspended transformation. The ease with which such a condition may be obtained or the persistence with which it may be maintained depends upon the general physical and chemical nature of the system as well as upon the particular phase reaction which has been suspended, and no entirely general treatment of the condition is yet possible. The suspended transformation, liquid → solid, is perhaps most commonly met and has been most fully studied.

Tammann[1] found that the crystallization, the occurrence of which ends the condition of suspended transformation, does not occur throughout the whole mass at once, but proceeds from one or more points that may be looked upon as nuclei. It is found that the number of such nuclei appearing per unit time in unit mass of the liquid increases at first with the degree of undercooling, reaches a maximum at some temperature and then decreases. The rate of crystallization not only depends upon the number of such nuclei, but is also dependent upon the passive resistance which the liquid offers to the propagation of the branches of the crystalline material; this passive resistance becomes greater as the temperature falls and the liquid becomes more viscous. At temperatures sufficiently below the melting point the number of nuclei will be small and the rate of crystallization enormously slow, so that the suspended transformation may continue almost indefinitely. This is the condition existing in the so-called amorphous solids, which are greatly undercooled liquids of high viscosity showing suspended transformation. Considering other types of suspended transformation, the change solid $\rightarrow$ liquid has not been observed to show such a condition in any one-component system. The transition solid $\rightarrow$ solid may be made to show suspended transformation either with rising or falling temperature or with rising or falling pressure, indeed the rigidity of the solid state is a property most favorable to slow transformation. The reactions liquid $\rightleftarrows$ vapor and solid $\rightleftarrows$ vapor in both directions are very liable to suspended transformation, as witness the phenomena of superheating of liquids and the undercooling of vapors which occur where nuclei of all sorts are carefully excluded. In general, suspended transformation is most easily limited or ended by introduction of a nucleus of the specific phase with respect to which the system is metastable, e.g., the missing solid for an undercooled liquid, but, as has been shown, the change may even then be indefinitely slow. Thus calcite has been shown to be the stable form of calcium carbonate under terrestrial conditions, but the occurrence in nature of the metastable form, aragonite, is sufficient indication of the slowness of the transformation.

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[1] *Z. physik. Chem.*, **25**, 441 (1898).

Experimental Methods for One-Component Systems: Space is not here available for discussing experimental methods in detail. Transition temperatures of two solids are most commonly determined by dilatometrical methods; i.e., by observing the change of volume of a solid with rise or fall of temperature, which will upon being plotted give a smooth curve up to the transition temperature, at which there is an abrupt change of volume with the formation of the new phase with its entirely different density. The transition temperature solid $\rightleftarrows$ liquid is more commonly determined by thermal methods, that is, by subjecting the system to the influence of a constant higher or lower temperature, which causes a regular increase or decrease of temperature to occur until the equilibrium temperature is reached; at this point the latent heat of fusion will hold the temperature constant until the change is complete. In the use of these, or any other of the many methods, suspended transformation must be prevented or compensated.

SYSTEMS OF TWO COMPONENTS

In passing to the study of systems classified as of two components, it will be well to consider briefly certain general facts as to the components, independent variables, and phases. As previously stated, a system belongs to this class if it is possible to express the composition of all the phases in terms of two substances, and not less than two. The haphazard choice, however, of any two pure elements or compounds from the laboratory shelves may not be depended upon to give merely a two-component system, but may also give rise to three-component systems, depending upon the nature of the substances taken. If the two substances employed give rise to no phases except such as are intermediate in composition between the two substances taken, the system will conform to the requirements for a two-component system; thus, the formation of solutions, which are always intermediate in composition between their components, introduces no new complication, nor does the formation of any *additive* compound from the two substances. Sodium sulfate and water, for example, may form, in addition to phases composed of the simple constituents, a solution of the two and may also form several hydrates, such as $Na_2SO_4.10H_2O$; the system is of two components, by application of the rule. If, on the other hand, the two substances form compounds other than those of an additive nature, the system cannot be regarded as of two components; e.g., bismuth nitrate and water form by hydrolysis phases consisting of basic nitrates, such as $2Bi_2O_3.N_2O_5.H_2O$, whose composition cannot be expressed in terms of bismuth nitrate and water nor of any other two substances derivable from them; the system is, therefore, of three components.

The independent variables in two-components systems are three in number, instead of the two considered in the case of one-component systems; in addition to the pressure and temperature, the composition of phases may also vary independently, through the formation of solutions. In order to make a complete representation of these three variables graphically, it is necessary to use diagrams in three dimensions, leading to surfaces and volumes in addition to the points, lines and areas occurring in two-dimensional representation. However, it is possible to study many of the relationships satisfactorily in two-dimensional graphs by choosing two of the three variables for representation, where the third is assumed constant or ignored because of its quantitatively small effect upon the equilibria. We shall therefore represent the conditions in this section by use of the three possible two-variable combinations, giving what are spoken of as p-t diagrams, p-c diagrams and t-c diagrams, where p, t and c stand respectively for pressure, temperature and composition.

In two-component systems we meet with a type of phase not occurring in one-component systems, namely, the *solution* phase. It lies in the nature of elementary instruction in chemistry that the student should in his introduction to chemistry obtain a somewhat restricted view of solutions; it lies in the phase rule to make clear how the term is of very broad significance, including many substances which may appear to be quite different. van't Hoff[1] has given a most satisfactory definition of the term solution: a solution is any phase the composition of which may vary continuously within certain limits. That a solution is a phase, and therefore homogeneous, excludes at once all mixtures, which are necessarily heterogeneous; that it may vary continuously in composition excludes elementary substances and compounds, each of which has definite composition. Such a classification of bodies into mixtures, elements, solutions and compounds is based upon homogeneity and composition and not upon the physical properties upon which the physicist's classification into solids, liquids and gases is made. Solutions may further be given a secondary classification on the basis of the physicist's three states of aggregation; there may be gaseous solutions, liquid solutions, and solid solutions. Gaseous solutions occur whenever any two gases are brought together, since all gases show unlimited solubility (a term to be defined later); liquid solutions are known popularly as well as by the chemist, and the term is applied to any homogeneous liquid where composition may be made to vary continuously, whether it has been prepared from a solid and a liquid like salt and water, a gas and a liquid like carbon dioxide and water, or substances in any initial physical state; and solid solutions, although less commonly met with, exist wherever the homogeneous phase has assumed a solid condition, as in the iron-carbon alloy known as steel. It is with these various types of solutions that we shall find our principal interest in the study of two-component systems.

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[1] van't Hoff, *Z. physik. Chem.*, **5**, 323 (1890).

By application of the phase-rule equation, it follows that for two-component systems, four coexisting phases give rise to invariant equilibrium, three coexisting phases to univariant equilibrium, two coexisting phases to bivariant equilibrium, and one phase to trivariant equilibrium. Trivariance is here possible, since variations in composition may occur in addition to variation in pressure and temperature. Of gaseous phases there can never be more than one present; of liquid phases, two is the maximum number thus far observed in coexistence; and of solids, there may coexist any number possible under the statement of the phase rule, consisting of pure components in their various polymorphic forms, of additive compounds, or of solid solutions. The number of possible equilibria is too great to admit of complete study in this chapter; the following table gives in the first column the five possible types of bivariant (two-phase) equilibria, which by formation of a third phase give rise to the univariant equilibria of column 2, and by addition of a fourth phase the invariant equilibria of column 3. The number of such types of phase complexes

TABLE XVIII

EQUILIBRIA IN TWO-COMPONENT SYSTEMS

Two-phase Equilibria (bivariant)	Three-phase Equilibria (univariant)	Four-phase Equilibria (invariant)
$V - L$	$V - L_1 - L_2$ $V - L - S$	$V - L_1 - L_2 - S$ $V - L - S_1 - S_2$, $V - L_1 - S - L_2$
$L_1 - L_2$	$L_1 - L_2 - V$ $L_1 - L_2 - S$	$L_1 - L_2 - V - S$ $L_1 - L_2 - S_1 - S_2$, $L_1 - L_2 - S - V$
$L - S$	$L - S - V$ $L_1 - S - L_2$ $L - S_1 - S_2$	$L_1 - S - V - L_2$, $L - S_1 - V - S_2$ $L_1 - S - L_2 - V$, $L - S_1 - L - S_2$ $L - S_1 - S_2 - S_3$, $L - S_1 - S_2 - V$
$V - S$	$V - S - L$ $V - S_1 - S_2$	$V - S - L_1 - L_2$, $V - S_1 - L - S$ $V - S_1 - S_2 - S_3$, $V - S_1 - S_2 - L$
$S_1 - S_2$	$S_1 - S_2 - L$ $S_1 - S_2 - V$ $S_1 - S_2 - S_3$	$S_1 - S_2 - L - V$, $S_1 - S_2 - L_1 - L_2$ $S_1 - S_2 - V - L$, $S_1 - S_2 - V - S_3$ $S_1 - S_2 - S_3 - S_4$, $S_1 - S_2 - S_3 - L$, $S_1 - S_2 - S_3 - V$

is here calculated with the restriction that the coexisting phases cannot include more than one vapor phase, nor more than two liquid phases. In columns 2 and 3 occur many repetitions of phase complexes; the total number of different systems is seventeen, of which five are bivariant, six univariant and six invariant.

The classification given shows the number of equilibria. The number of specific equilibria in a given system may, however, be much larger through the occurrence of many different solid phases; thus the univariant type equilibrium $V - L - S$ may occur in as many specific forms as there are solid phases possible to be substituted for S. In our study of these extensive possibilities our method will be to consider each of the five bivariant equilibria in turn, with such of the univariant and invariant equilibria derivable from them as have special interest.

A. THE EQUILIBRIUM; GAS-LIQUID

The equilibrium between a gas and a two-component liquid, known as a binary solution or less happily as a binary mixture,[1] has a variance of two; the vapor pressure of such a system therefore depends upon the composition if the temperature be kept constant, or upon the temperature if the composition be kept constant. If the two components possess unlimited mutual solubility, the composition may be made to vary from 100 per cent of one component to 100 per cent of the second, and a continuous vapor pressure curve at constant temperature may be drawn. As to the exact nature of this dependence of vapor pressure upon composition, the phase rule gives no information; much more satisfactory treatment is possible according to the theory of the liquid state, leading to a treatment of the important process of fractional distillation. It has also been shown in an earlier section that the distribution law (Henry's law) gives a satisfactory basis for treatment of the equilibrium gas-liquid. A phase-rule treatment of such two-phase systems will not be given here.

If a system, gas-liquid, is submitted to such conditions that a second liquid phase appears, there are features of interest in the new univariant equilibrium which results ($V - L_1 - L_2$). Leaving to a later section a more complete discussion of the limited or restricted solubility that must characterize the liquids, let us simply assume that we have such a pair of liquids in equilibrium with their vapor, and let us keep in mind that each of the liquids contains both components, since it is an empirical rule that solubility of liquids, if it occurs at all, is always mutual. In Fig. 10 is given a $p - c$ diagram of such a system, in which we assume a constant temperature; the varying compositions are shown on the axis AB and the pressures on the ordinate AC. The vapor pressure of the pure component A is represented by the point C. Let us assume that addition of component B lowers the total pressure of the system; if, as sometimes happens, the total pressure increases instead of diminishing on addition of B, the detail only of the diagram will differ from Fig. 10, the essentials remaining the same. The curve CE is then a part of the curve of the total vapor pressure of the system. At the point E we reach the saturation concentration of the liquid, represented by the composition x, and further addition of B gives rise to a new liquid phase of the composition y. We now have two liquid phases and vapor at a fixed temperature, and the system is isothermally invariant; that is, no changes in pressure or composition can occur so long as the temperature is kept constant and the three phases are retained. Addition of B therefore increases only the mass of the second liquid y. Turning attention to the vapor pressures, since the liquid x, the liquid y and vapor are in equilibrium with each other, the liquid y must have the same vapor pressure as x, namely p_t; both its pressure and composition are therefore fixed by the point F. Any relative quantities of A and B taken so as to give a total composition between x and y can give only x and y as solutions and a total pressure p_t. When the amount of B is increased so that the composition falls to the right of y, the phase x disappears and the vapor pressure falls along the curve FD, which terminates at D, the pressure of the pure component B. The total vapor-pressure curve therefore consists of two discontinuous parts, CE and FD, connected by a line of invariant pressure. In the metastable region $E - F$ the curve is believed to exhibit a minimum and maximum (G and H) and a point of inflexion O, like the pressure-volume curve for a pure liquid below its critical temperature, as shown by van der Waals; using the reasoning made familiar there, the curves EG and HF are to be regarded as metastable and GOH as unrealizable. The familiar theory of van der Waals, as applied to a pure liquid, has been extended so as to cover the case of a binary liquid solution.[1] The complete curve here drawn is the curve for the composition of the liquid phases; that for the composition of the vapor phase, which would fall below $CE - FD$, is not here indicated.

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[1] The use of the term "mixture" for a homogeneous solution is to be deplored, since it is a term implying heterogeneity, and therefore confuses the essential phase relations. In this chapter effort will be made to avoid the use of the word mixture and all its derivatives except where heterogeneity is actually present; on account however of prevalent usage, it will occasionally be necessary to refer to the less desirable nomenclature.

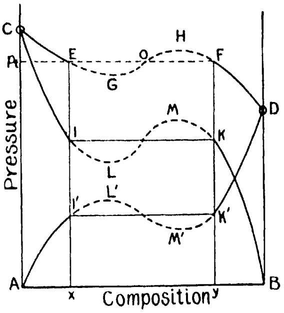

FIG. 10 p-c. Diagram for Liquid-Vapor Equilibrium, Two Component System

Passing to the partial pressures of the individual components in the system, the curve for the partial pressure of A must begin at C and must reach the level of zero pressure when A is absent, that is, must end at B. The interrupted curve CI-KB shows its course. The points I and K possess special interest. The vapor pressure of A in the solution x must be the same as in the solution y, since otherwise a distillation from phase x to phase y would occur. It follows then that the pressure of A in the phase in which it predominates (x) is in nowise different from its pressure in the phase in which it is present in but small amounts.

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[1] van der Waals and Kohnstamm *Lehrbuch der Thermodynamik*, 1800.

This fact becomes still more striking if one considers pairs of liquids in which the mutual solubility is very low, as in benzene and water; here, the solubility of water in benzene at 25° is only .07 per cent[1] and that of benzene in water is of the same order, so that the points *x* and *y* very nearly coincide with *A* and *B*; yet the vapor pressure of benzene in the phase containing only about 0.1 per cent benzene is exactly equal to that in the phase containing 99.93 per cent benzene, that is, practically as high as that of pure benzene. This was first demonstrated experimentally in the case of ether and water by Konowalow.[2]

It is of value to keep this relationship in mind, so that the error may not be made of carrying over into the realm of concentrated solutions ideas based upon the theory of dilute solutions, according to which the vapor pressure is lowered in proportion to the molecular concentration of the second component. Expressing the condition in the general language of Gibbs' concept, the chemical potential of a component in two phases at equilibrium is the same in the dilute phase as in the concentrated phase.

What has been said for the curve *CI–KB* applies equally to the partial pressure curve for *B*, namely *DK′–I′A*. The metastable and labile sections between *I* and *K* and between *I′* and *K′* represent the same conditions as in the curve for total pressures.

B. THE EQUILIBRIUM; LIQUID-LIQUID

The existence of two liquid phases in equilibrium implies a limited mutual solubility; where the solubility is unlimited, such a system cannot exist. A complete theory on which to forecast the extent of mutual solubility is not known; the topic will be treated in the third section of this chapter. It is possible however to arrange classes of substances, both liquid and solid, in an order representing in a rough way their solubility relations; the key to it is expressed in the phrase which has come down from the alchemists, *similia similibus solvuntur* (like is dissolved by like). Our selection of partially soluble liquids will therefore necessarily give us components which are quite dissimilar in composition, in general chemical properties, and particularly in such physical properties as degree of association and dielectric constant.

Upper Consolute Temperatures: Phenol and Water: When phenol and water are brought together at room temperature and in suitable proportions, two liquid phases result together with a vapor. This has become a classic instance of a two-liquid system. In studying it, we shall treat it as a condensed system, in view of the fact that changes of pressure (within reasonable limits) have but slight effect upon the equilibrium existing between the liquids; omitting therefore the vapor phase from reference and substituting a fixed pressure, we have a univariant system in which the relationship of temperature and composition will be studied. Alexejew,[3] to whom, with Guthrie, we owe the pioneer work on two-liquid systems, was the first to obtain a clear picture

[1] Hill, *J. Am. Chem. Soc.*, **45**, 1154 (1923).

[2] *Wied. Ann.*, **14**, 219 (1881).

[3] *Wied. Ann.*, **28**, 305 (1886).

of the relations of these components; many others[1] have since added to the data on this system, and Rhodes and Markley[2] have recently completed the diagram, showing the relations of the liquids with the various solid hydrates and with ice. The two liquid phases formed at room temperature differ in that one of them is water with a small proportion of phenol and the second is chiefly phenol with a small proportion of water; as the temperature rises, the proportion of phenol increases in the aqueous phase and the proportion of water increases in the phenol phase, until, at 68.4°, the two liquid phases have identical composition. Table XIX contains figures taken from Rothmund's experiments.

TABLE XIX

THE SYSTEM: PHENOL-WATER

Temperature	Wt. Per Cent Phenol in Phase L_1	Wt. Per Cent Phenol in Phase L_2
10°	7.5	
20	8.5	72.2
30	8.7	69.9
40	9.7	66.8
50	12.0	62.7
55	14.2	60.0
60	17.5	56.2
65	22.7	49.7
68.4	36.1	36.1

The above data are plotted in Fig 11. At any fixed temperature, such as 20°, the composition of the two liquid phases is necessarily fixed, the system being invariant, and the points are indicated by A and A'; the isothermal line joining them is spoken of as a *tie-line*, and the two solutions are called conjugate solutions.

If now, at this temperature, 50 per cent each of phenol and water are brought together, the composition of the complex will be represented by the point x, the complex will form two liquids of the compositions A and A'. The relative quantities of these phases formed may be calculated geometrically from the diagram, the weight of phase A formed will be the fraction $\frac{xA'}{xA' + xA}$ of the total, and that of A' will be $\frac{xA}{xA' + xA}$ so that the ratio of the weights of A to A' will be that of the lines xA' to xA, the weight of each is inversely proportional to the displacement of its composition from the composition of the total complex.

The effect of rising temperature upon this system is to increase the mutual solubility: the curve $A'B'C$ shows an increase in the concentration of phenol and the curve ABC an increase in that of water. At the point C, the curves merge into each other without discontinuity, and we have a critical state in the sense in which critical states have been defined above. What have been

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[1] Paterno and Ampola, *Gazz. chim. ital.*, **27**, I, 481 (1897); Rothmund, *Z. physik. Chem.*, **26**, 433 (1898); Schreinemakers, *Z. physik. Chem.*, **29**, 579 (1899), Scarpa, *J chim. phys.*, **2**, 447 (1904); Rozsa, *Z. Elektrochem.*, **17**, 935 (1911); Smits and Maarse, *Proc. Acad. Sci. Amsterdam*, **14**, 192 (1913).

[2] *J. Phys. Chem.*, **25**, 527 (1921).

conjugate solutions at lower temperatures have now become a single soluti the temperature at which this phenomenon occurs is called the consolute temp ature, or critical solution temperature (t_c). At higher temperatures, water an phenol are mutually soluble in all proportions, and the system can consist but one liquid phase; below the consolute temperature, the mutual solubilit is limited. No solution therefore can exist having composition indicate by points within the area A-B-C-B'-A', but such compositions can lea only to two conjugate solutions of composition lying upon the curves at th intersections with the isothermal tie-lines.

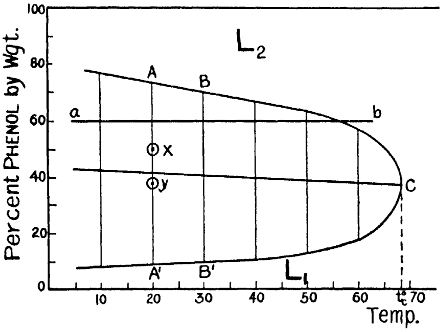

FIG. 11. *t.-c.* Diagram for the System Phenol-Water

The phenomena occurring at the consolute point are worth considering. Assume complex y of the critical composition (36.1 per cent phenol) to be prepared at room temperature; it will yield two liquid phases of not very widely different weights. If the temperatur is slowly raised, the quantities of the two phrases will vary slightly but not to any large extent as can be seen from the diagram. If this system be stirred briskly, it will assume the characteristic milky appearance of an emulsion, always settling, however, into two clear phases When the temperature 68.4° is reached, the turbidity vanishes sharply, so that the liqui is quite transparent, the passage from opacity to transparency is so definite that the temperature can be noted to 0.1°, and sometimes to 0.01°. If now the transparent liquid at a highe temperature is allowed to cool, the operations are reversed, and the turbid emulsion appear again at the consolute temperature.

If instead of a 36.1 per cent phenol-water complex, some other is taken and warmed a series of changes occurs which has a superficial likeness to what has just been described but must be sharply differentiated from the true critical changes. Assume a complex containing 60 per cent phenol to be warmed from 10° to 70°; the process can be followed by drawing a line of equal concentrations, *ab*, called an *isopleth*. At 10° the system will consist of about 4/5 of the phenol-rich phase lying at the bottom of the vessel used and 1/5 of supernatant aqueous layer, as can be calculated from the intercept of *ab* with the 10° isotherm. As the temperature is raised to 20°, 30°, etc., the quantity of the upper layer will diminish noticeably; if the system is stirred, it will be turbid, but will always settle into two transparent layers. After each rise of temperature, stirring and subsidence, the line of separation between the phases will be found nearer the upper surface; at 55°, the liquid will no longer show turbidity and the line of separation has reached the surface We have passed from a two-liquid system to a one-liquid system; but we have *not* passed through a critical state. What is occurred has been merely the disappearance of a phase, what is required for a critical state is that two phases should become identical. It is only with the critical composition (in this system 36.1 per cent of phenol) that a critical state can be reached, with all other compositions, one phase increases at the expense of the other until the second has disappeared In experimental practice, the distinction is not hard to observe, if the critical composition has been taken, the two phases will be *equal* in weight and volume just below the temperature at which they appear and disappear, as will be seen by marking a point just inside C′ and drawing a perpendicular (an isotherm) through it. On the other hand, for any other composition the two phases will be extremely unequal at a temperature just below that at which they appear, the new phase will appear as a mere drop or two at the top or the bottom of the container.

Systems like the one discussed above are said to possess an upper consolute temperature. A few generalizations for systems of this type may be made. The curve which represents the boundary of the two-liquid area, or the curve of conjugate solutions, is a continuous curve; its tangent at the consolute temperature is perpendicular to the temperature axis. The curve bears a resemblance to a parabola, but a generalized equation that should fit all cases has not been found. In general, the curve shows the largest changes in composition within a comparatively few degrees below the consolute temperature; in the case studied, the two liquids depart from each other by 27 per cent within the temperature range 68.4° to 65°. It has been found that a rough approximation to a "law of the straight diameter"[1] exists, that is, that a line connecting the middle points on the tie-lines, *A*-*A*′, *B*-*B*′, etc., is a nearly straight line as shown by *Cc* in Fig. 11. This relationship suggests at once the law of Cailletet and Mathias[2] for the densities of a liquid and its vapor approaching the critical state, and strengthens the analogy between the critical phenomena here discussed and those occurring in a liquid-vapor system. The statement is only an approximation, however, if the composition is expressed in molar fractions instead of per cent by weight, the curvature of the diameter becomes pronounced.[3] There is also to be noted, in systems showing consolute temperatures, a most interesting phenomenon in the area immediately above and around the critical point: the liquid, though plainly transparent, has a bluish haze, spoken of as the critical opalescence, which has occasioned much interest.[4] Although an optical condition of this sort might at first be thought to indicate heterogeneity, Smoluchowski[5] has shown that the optical effect is due to the scattering of light not by individual particles but by local variations of density arising from very slight inequalities in temperature. This critical opalescence, far from interfering with the experimental determination of the consolute point, has been found to be most helpful in indicating a close approach to the critical region.

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[1] Rothmund, *Z. physik. Chem.*, **26**, 433 (1898)

[2] *Compt. rend.*, **102**, 1202 (1886).

[3] Menschutkin, *J. Russ. phys. chem. Ges.*, **44**, 1137 (1912), Aten, Roozeboom's Die heterogenen Gleichgewichte, 2, II, p. 61 (1918)

[4] Ostwald, *Lehrbuch*, II, 2, p. 683 (1902), Rothmund, *Z. physik. Chem.*, **26**, 433 (1898); Guthrie, *Phil. Mag.*, (5) **18**, 504 (1884), Friedlander, *Z. physik. Chem.*, **38**, 385 (1901), Timmermans, *ibid.*, **58**, 129 (1907); Konowalow, *Ann. Physik.*, **10**, 360 (1903).

[5] Smoluchowski, *Ann. Physik*, **25**, 205 (1908)

The use of the terms solvent and solute in the case of two-liquid phases will be seen to be both inept and useless; no fundamental distinction between the function of the phenol and that of the water is known to exist, and certainly we cannot rightly regard one component as active and the other passive, as the words imply. Where we have in equilibrium two phases, of which one is of fixed composition and one of varying composition, as in the case of solid sodium chloride and its aqueous solution, it is a convenient usage to call the phase of fixed composition the solute and the component occurring only in the solution the solvent. If we have such a system as $Na_2SO_4.10H_2O$ and its aqueous solution, it is not easy to tell why we often speak of Na_2SO_4 as the solute; certainly no general definitions of the terms are possible.

The number of two-liquid systems showing an upper consolute temperature is considerable; a few of these will be given later in Table XXII.

Lower Consolute Temperature: Tri-ethyl Amine and Water: In a certain number of cases, the solubility curves for two-liquid phases approach each other with diminishing temperature, and meet at a lower consolute temperature which is analogous to the upper consolute temperature discussed previously. Tri-ethyl amine and water were found by Rothmund[1] to show this behavior. The data for this system follow.

TABLE XX

THE SYSTEM. TRI-ETHYLAMINE-WATER

Temperature	Wt. Per Cent Amine in Phase L_1	Wt. Per Cent Amine in Phase L_2
70°	1.6	—
50	2.9	—
30	5.6	96
25	7.3	95.5
20	15.5	73
18.5	about 30	about 30

Fig. 12 is the plot of these figures. It will be noted that the curve is quite extraordinary; the mutual solubilities are very small at all temperatures above 25°, but increase enormously from 25° to 18.5°. The curve is, finally, nearly perpendicular to the temperature axis; as a result, while it was not difficult to obtain the consolute temperature with considerable accuracy, the corresponding composition is not at all accurately known. The observation of the critical opalescence, which is most pronounced when closest to the consolute point, indicates that the composition is not far from 30 per cent.

Most of the other substances showing lower consolute temperatures are amines, and therefore not easy to bring to a high state of purity; since the presence of a third component has been shown[2] frequently to have a very pronounced effect upon the consolute temperature, it is possible that the figures for this class are less accurately known than those of the previous class. In none of these latter instances is the law of the straight diameter even approximately applicable.

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[1] *Z. physik. Chem.*, **26**, 433 (1898).

[2] Timmermans, *Z. physik. Chem.*, **58**, 187 (1907); Friedländer, *Z. physik. Chem.*, **38**, 385 (1901); Dolgolenko, *Z. physik. Chem.*, **62**, 499 (1908); Crismer, *Bull. Acad. Sci.*, **30**, 97 (1895).

Completely Closed Solubility Curves: Nicotine and Water: With a knowledge of solubility curves closed at higher temperatures and others closed at lower temperatures, it is natural to look for cases where the curves are closed at both temperatures, i.e., systems with both upper and lower consolute temperatures. Hudson[1] was the first to discover such an example in nicotine and water; Tsakalotos[2] confirmed the data of Hudson within a few per cent. In Table XXI are given, not the two conjugate compositions for a fixed temperature, but the two temperatures corresponding to a fixed composition; this follows from the isoplethal method of experimentation used by Hudson which will be described later. Either method will give a complete set of points by which the entire closed curve may be plotted. Fig. 13 represents the curve.

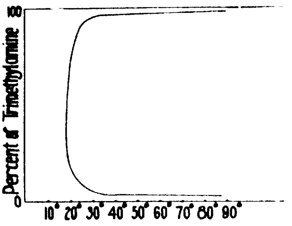

Fig. 12 t-c. Diagram for the System, Triethylamine-Water

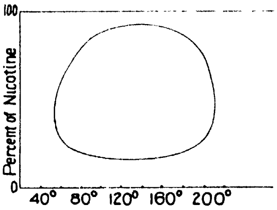

Fig. 13 t-c Diagram for the System, Nicotine-Water

TABLE XXI

The System: Nicotine-Water

Per Cent Nicotine by Weight	Lower Temperature	Upper Temperature
6.8	94°	95°
7.8	89	155
10.0	75	--
14.8	65	200
32.2	61	210
49.0	64	205
66.8	72	190
80.2	87	170
82.0	129	130

Tsakalotos finds that the composition for both critical points is the same, namely, 34 per cent of nicotine, the lower temperature is 60.8°, the higher 208°. Between these temperatures two conjugate liquids may be obtained, beyond them, or, in general, outside of the closed curve, only one is possible, and the liquids are completely soluble.

A completely closed curve, such as that of Fig. 13, must have points of maximum and of minimum solubility. At these points the tangents to the curve are parallel to the temperature axis. Applying van't Hoff's law of mobile equilibrium, from the fact that at these points the solubility does not vary with the temperature, it follows that the heat of solution is zero. Beginning at each such point the curve rises with rising temperature in one direction and falls with rising temperature in the other; the branch which shows a rise with the temperature, that is, possesses a positive coefficient of solubility, represents solutions in which the heat of solution is negative, and vice versa for the other branch.

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[1] *Z. physik. Chem.*, **47**, 114 (1903).

[2] *Bull. soc. chem.*, **5**, 397 (1909).

The preceding table gives the critical data for some of the types of systems discussed above.[1]

Conjugate Liquids Without Consolute Points: There is a very large number of conjugate liquid pairs which possess neither an upper nor a lower consolute temperature. This is the case with ether and water and with chloroform and water; it is probably the case with any pair whose mutual solubility is very low. As temperatures are lowered in such cases, a point is reached at which a solid phase appears; where water is one of the components, this occurs not far below 0°, since the concentration of the second component in the water and its effect upon the freezing point are small. There are, therefore, four phases present $(S - L_1 - L_2 - V)$ and the system is invariant; if subjected to a cooling environment, ice continues to form until the aqueous layer has completely disappeared, and the system of conjugate solutions cannot exist at any lower temperature. The exact relations will be shown in a later paragraph. If, on the other hand, the temperature be raised, a point will finally be reached at which one of the liquids, namely, that one rich in the more volatile component, is at its critical state; the vapor above it has reached not only the same relative composition as the liquid phase, but also the same density, and the two-component liquid phase disappears in the same fashion as at the critical temperature for a one-component system. Ether and water are known to behave thus.

At −3.83° the solid phase appears,[2] and below this temperature only the ethereal liquid phase exists. At this temperature the ethereal phase contains only about 1 per cent of water, and the increase with temperature rise is very small, the aqueous phase contains 12.7 per cent ether, but has a negative solubility coefficient, so that the ether content has fallen to 5.34 per cent at 30°, at 82°, it has fallen to 2.7 per cent.[3] Kuenen[4] and Robson have found that at 201° the ethereal phase, which contains about 2 per cent of water, reaches its critical state, above which only the water phase can exist as a liquid. Generalizing from the behavior of this system, we may say that where a system of conjugate liquids does not show an upper nor a lower consolute temperature, it terminates at low temperatures with the disappearance of the phase rich in the component of higher melting point, and at higher temperatures through the disappearance of the phase rich in the more volatile component at a critical point for the system liquid-vapor.

[1] For a fairly complete list of known cases, see Roozeboom's Die heterogenen Gleichgewichte, 2, II (Aten), pp. 70, 73, 74, 76, 78, 81. To these add Keyes and Hildebrand, *J. Am. Chem. Soc.*, **39**, 2126 (1917); McKelvey and Simpson, *ibid.*, **44**, 105 (1922); Kraus et al., *ibid.*, **44**, 1249 and 1949 (1922).

[2] Hill, *J. Am. Chem. Soc.*, **45**, 1143 (1923), this article contains a bibliography of the system.

[3] Klobbie, *Z. physik. Chem.*, **24**, 615 (1897).

[4] *Z. physik. Chem.*, **28**, 342 (1899).

TABLE XXII

Critical Data for Two-Liquid Systems

Systems Having Upper Consolute Temperatures			Systems Having Lower Consolute Temperatures		
Substances	Wt. Per Cent of First-named Component	Consolute Temp.	Substances	Wt. Per Cent of First-named Component	Consolute Temp.
Methyl alcohol-hexane [1]	30.1	42.6°	Carbon dioxide-o-nitrophenol [7]	72	23°
Succinic nitrile-water [2]	51	55°	Di-ethyl amine-water [8]	13	143°
Carbon disulfide-methyl alcohol [3]	85	35.7°	β-Collidine-water	4	6°
Aniline-hexane [4]	52	59.6°	1-Methyl piperidine-water [9]	5	48°
Benzene-sulfur [5]	35	163°			
Aluminum bromide-[6] sodium bromide	92	232°			

Systems Having Both Upper and Lower Consolute Temperatures

Substances	Wt. Per Cent of First-named Component	Lower Consolute Temp.	Wt. Per Cent of First-named Component	Upper Consolute Temp.
Methyl ethyl ketone-water [10]	31	−6°.	20	133°
β-Picoline-water [11]	7	49°	9	153°
αα-Lutidine-water [11].	7	45°	10	164°
3-Methyl piperidine-water [11]	4	56°	8	236°
4-Methyl piperidine-water [11].	5	85°	8.5	189°
2-Methyl piperidine-water [12]	4	79°	6	227°

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[1] Rothmund, *Z. physik. Chem.*, **26**, 433 (1898).

[2] Schreinemakers, *Z. physik. Chem*, **23**, 439 (1897).

[3] McKelvey and Simpson, *J. Am. Chem. Soc.*, **44**, 105 (1922).

[4] Keyes and Hildebrand, *J. Am. Chem. Soc.*, **39**, 2120 (1917).

[5] Alexejew, *Wied. Ann.*, **28**, 305 (1886).

[6] Kendall, *J. Am. Chem. Soc.*, **45**, 968 (1923).

[7] Buchner, *Z. physik. Chem.*, **30**, 665 (1906).

[8] Lattey, *Phil. Mag.*, **10**, 397 (1905).

[9] Flaschner, *Z. physik. Chem.*, **62**, 493 (1908).

[10] Timmermans, Roozeboom's Die heterogenen Gleichgewichte, 3, II, p. 76.

[11] Flaschner, *J. Chem. Soc.*, **95**, 668 (1909).

[12] Flaschner and McEwen, *ibid*, **93**, 1000 (1908).

Space does not permit a study of two-liquid systems in which the pressure is treated as a variable. Suffice it to say that, in accordance with Le Chatelier's theorem, pressure must increase mutual solubility where solution is accompanied by a diminution in volume, and decrease solubility in the infrequent cases where an increase in volume occurs. The effects upon the solubility are usually of small order. In a number of cases high pressures have, however, altered the location of consolute points considerably.

Experimental Methods: The most commonly used method for determining the mutual solubility of two liquids is that devised by Alexejew[1]; it consists in introducing known weights of the two liquids into a small glass tube, which is then sealed and rocked in a bath in which the temperature rises slowly; the temperature at which the two-phase emulsion becomes clear gives a point on the curve, which may be confirmed by cooling the clear liquid until it becomes turbid. A series of such points will give the complete outline of the curve, as shown above in the data for nicotine and water. Regarding the system as a condensed system, the effect of the pressure within the tube may be neglected. This extremely useful method of experimentation, called by Rothmund[2] a synthetic method, may be more properly classified as *plethostatic*,[3] since it consists in using a system of fixed composition and determining the temperature at which conjugate liquids appear. *Thermostatic* methods are those in which the temperature of a system is fixed, and the composition of the two liquids subsequently determined after sufficient agitation has brought them to equilibrium; this can occasionally be done by direct analysis, though usually liquids do not lend themselves to easy analysis. A thermostatic method, dependent upon volumetric measurements,[4] consists in weighing the two components into each of two vessels in differing amounts, and determining the volumes produced after equilibrium has been obtained at a fixed temperature; graduated cylinders may be used in place of more accurate apparatus.

Let m and m' represent the weights of the first component used in the two experiments; let x represent its concentration in grams per cubic centimeter at equilibrium in the upper phase in both experiments, since by the phase rule the concentration at saturation cannot vary; and, similarly, let y represent its concentration in the lower phase in both experiments. If, now, the measured volumes of the upper phase are a and a', and the volumes of the lower phase b and b', it follows that $ax + by = m$, and $a'x + b'y = m'$.

Solving the equations for x and y will give the concentration of the first component in each phase, expressed in g. per cc. of solution. If the equations are again solved, substituting in place of m and m' the weights n and n' of the second component, its concentration in each phase becomes likewise known in the same units. By adding together the weight of each component present in 1 cc. of a given phase, the weight per cubic centimeter, or density, is obtained, and the percentage composition by weight thus follows. A single pair of experiments will, therefore, give the solubility in unit volume and in unit weight. This procedure involves no assumptions as to changes of volume occurring.

In addition to plethostatic and thermostatic methods, *barostatic* methods are conceivable; none have been devised.

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[1] *Wied. Ann.*, **28**, 305 (1886).

[2] *Z. physik. Chem.*, **26**, 443 (1898).

[3] Hill, *J. Am. Chem. Soc.*, **45**, 1143 (1923).

[4] Hill, *loc. cit.*

C. The Equilibrium: Solid-Liquid

In passing to systems of two components in which solid phases are considered, the relations differ markedly according as such phases consist of pure components, compounds, or solid solutions The classification which will be used in the effort to give as complete a treatment as possible within short space is as follows:

- I. The solid phases consist of pure components only.
  - (*a*) Only one liquid phase appears; i e., the fused components have unlimited solubility.
  - (*b*) Two liquid phases appear; i.e , the fused components have limited solubility.
- II. The solid phases consist of compounds.
  - (*a*) The solids show transition points, but no melting points.
  - (*b*) The solids show melting points, called congruent melting points.
- III. The solid phases consist of solid solutions.
  - (*a*) Only one solid solution forms; i e., the solids show complete mutual solubility.
  - (*b*) Two solid solutions form; i e., the solids show limited mutual solubility.

Ia. Pure Components as Solid Phases, with a Single Liquid: We shall develop a diagram of an entirely general nature for this case and afterward show that it indicates, at least qualitatively, relations which are met with in some of our commonest laboratory experimentation, such as the determination of melting points and of the solubilty of solids in liquids, as well as in important commercial operations, such as the manufacture of metallic alloys. Treating our systems as prepared under the pressure of their own vapor, or under atmospheric pressure, and omitting the vapor phase from consideration, we may use Fig. 14 to represent the temperature-composition relations of the system $S_1 - S_2$. Here the point *R* represents the freezing point of pure S_1; as increasing quantities of S_2 are added, the freezing point falls along the curve *RC*, which therefore represents the equilibrium of *S* with the liquid phase. In like manner *M* is the freezing point of S_2 and *MC* its freezing-point curve. Since in all cases the freezing point of a component which exists in the solid phase in pure condition is lowered by the presence of a second component in its solution, the two curves must take the general direction here indicated and must intersect at some point *C*, which will be discussed later; our freezing-point diagram therefore must show discontinuity, and the two branches to the curve represent respectively S_1 as solid phase in equilibrium with liquid and S_2 as solid phase in equilibrium with liquid. The two curves have been spoken of as freezing-point curves; they are also correctly named solubility curves, since they represent the concentration of the solutions saturated with a given phase at a given temperature, which is a definition of solubility. It is worth emphasizing that there is no distinction of any sort between a freezing-point curve and a solubility curve since each represents the temperatures and compositions for the equilibrium between solid and liquid. Most of our solubility data in the literature represent simply sections of the general curve *CR* or *CM*. It is also worth noting that in a two-component system of this type there is qualitative equivalence in the functions of the two components; that is, one is the solid phase through a part of the range of composition, and the other through the remainder.

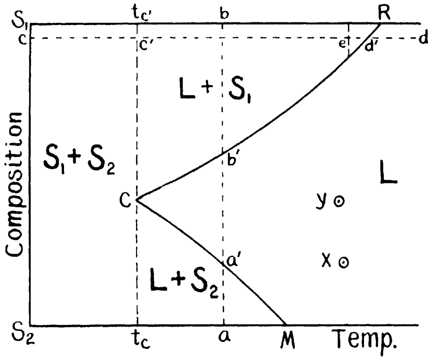

FIG. 14. The System $S_1 - S_2$. The Solid Phases are Pure Components, with one Liquid Phase Present

The diagram for a solubility curve such as *CR* is here given in its simplest form; it will frequently show wide variations from the simple form indicated here, the only unvarying condition being that it necessarily begins at the point of intersection *C* and ends at the melting point *R*. It may, for example, show a discontinuity in direction at some intermediate point; as previously stated, this is evidence of a change of phase and must represent (since compound formation is here left out of discussion) that the solid phase has a transition point from one polymorphic form to another. The curve for the equilibrium of silver nitrate (solid phase) and water shows such a transition point at 160°; that for ammonium nitrate (solid phase) and water shows breaks at 32°, 82.7°, and 125.6°. Moreover, the curve sometimes fails in part of its course to maintain its slope toward the axis of the solid component with temperature rise. A slope in this direction means an increase in solubility with rising temperature; but numerous instances exist in which the solubility decreases with rising temperature, well-known cases being calcium chromate in water and calcium citrate in water. Maximum and minimum points in the solubility curve are also by no means uncommon. All of these directions and changes of direction can be derived from van't Hoff's law whenever the thermal data are available; the solubility curve is ascending at a given point when the heat of solution in the saturated solution is negative at that point, is descending when the heat of solution is positive at that point, and is neither ascending nor descending (which is the condition at a point of maximum or minimum solubility) when the heat of solution is zero. In applying this law, however, it is necessary to remember that the heat of solution which governs the direction of the equilibrium by its sign is the heat of solution at *saturation*, i.e., the heat developed by the last increment entering the solution. Van't Hoff's law has to do with a displacement of an equilibrium by thermal means; it is clear that what may happen in a system not yet in equilibrium (i.e., not yet saturated) is altogether irrelevant. A recollection of this method of applying the law is essential if one is to avoid error. For example, it is common knowledge that when water is poured upon solid potassium hydroxide, much heat is evolved; if one deduced therefrom that the solubility of the compound decreased with the temperature, the error would be flagrant. The initial heat of solution is positive; it may be that the total heat of solution is positive; but the final heat of solution, representing the dissolving of the last increment entering the solution at the saturation point, is negative, and hence a rise of temperature will result in the dissolving of another increment.

Returning to Fig. 14, a solubility curve such as CR represents saturation or equilibrium conditions, it separates two regions in which solutions may occur, stable or metastable. The area to the right of the curve CR is the region of unsaturated solutions, that to the left is the region of metastable supersaturated solutions. A phase-rule distinction between these three types of solutions is not only simple, but is the only logical one. A saturated solution is one in equilibrium with the solid phase, and is therefore unaffected by addition of more solid phase, an unsaturated solution is one which will dissolve more solid phase if it be added, and a supersaturated solution is one which, being metastable, will precipitate solid phase from its own composition and fall to the point of saturation if a nucleus of the solid phase be added. All concepts of degrees of saturation must always refer to a particular solid or saturating phase (S_1 in the case of the curve CR), since a solution in equilibrium with one phase is quite capable of entering into new relations of saturation with respect to some second phase.

The intersection of the two-solubility curves (C), called the *eutectic point*, is the most interesting point of the diagram. Since the curve RC represents solutions saturated with S_1, and MC solutions saturated with S_2, the intersection must represent a solution saturated with both solids. The system represented by this point consists of two solid phases, solution and vapor, and is called a quadruple point; by the phase-rule equation, it is an invariant point. A solution to be in equilibrium with both solids can have therefore only the eutectic composition C and can exist in stable equilibrium only at the eutectic temperature, t_c. Rise of temperature above t_c results in the disappearance of one or both solid phases, and fall of temperature in the disappearance of the liquid. The eutectic point may be defined in terms of these phenomena; it is an invariant temperature at which the phase reaction of the system, upon removal of heat without change of temperature, results in the disappearance of the liquid phase.

In a system including a eutectic we have a simple and widely used means of securing a constant temperature. If two solids, properly chosen as to their solubility relations, are brought together in the eutectic proportion or any proportion approximating the same, they will begin the process of dissolving which, being endothermal in all common cases for both solids, reduces the temperature to the eutectic temperature. If, now, the system is well enough insulated so that heat can reach it from without only at a moderate rate, and is well stirred so that solution of the solids can occur quickly and temperature inequalities be eliminated, it will remain constant at the eutectic temperature until one of the solids has dissolved completely. With proper apparatus, extremely constant temperatures result; but, as pointed out in our introduction, it does not follow that the equilibrium will be reached at all if the apparatus is unsuited. Thus, the eutectic temperature for sodium chloride and water is – 22.4°, and a coarse mixture of the two solids, ice and salt, gives a reasonably effective freezing mixture for the household ice-cream freezer; but it is doubtful if this mixture, poorly insulated from the outside and warmed from the inside, practically free from stirring and with the salt and ice poorly mixed, ever gets within many degrees of – 22°; that is, no equilibrium is reached. But, if snow and fine salt be put in a Dewar flask and well stirred, a perfectly constant temperature may be maintained for hours; equilibrium is really attained. Examples of other eutectic temperatures and compositions will be given later in Table XXVIII, together with eutectics of other classes.

The existence of eutectics for systems of salts and water was first observed by Guthrie.[1] At first, in the absence of knowledge of the phase rule, incorrect interpretations were made. The solid separating out was thought to be a compound, and was called a cryohydrate, the point being named the cryohydric point. The view that the solid was a compound was based upon its constant composition; for, it will be seen (Fig. 14) that if the solution *C* deposits solid by abstraction of heat and at the same time itself remains unchanged in composition, as the phase rule requires for an invariant point, the solid precipitated must be of the same composition as the liquid and will therefore also have an unvarying composition; reversing the process and warming this solid material, it will melt at a constant temperature, which is likewise the behavior of a pure compound. The fact that the solid is not a compound, but a mixture of solid phases, was shown by Pfaundler[2] and Ofer[3] who showed the identity of the physical properties of this material with those of a mixture; heterogeneity can sometimes be detected by careful direct examination, and always by means of microscopical examination. Constancy of composition and constancy of melting point alone, it will be seen, cannot establish a chemical compound; the application of the phase rule (here nothing more intricate is involved than the intersection of two lines) is, however, adequate to settle the question. It will later be shown that the evidence of the phase rule may be not only negative as to compound formation, as in this instance, but may also be positive.

The general diagram of Fig. 14 may be used to illustrate the effect of isothermal and isoplethal changes. Assume that pure component S_2 be taken at some temperature, a, below the melting points of both compounds and that S_1 be added to it continuously at constant temperatures; the isotherm ab will indicate, by its intersections, all the changes which occur. Addition of solid S_1 will produce at once a small amount of solution of the composition a', in equilibrium with S_2, as indicated by $a'a$, serving as a tie-line between the liquid and solid, which bear a conjugate relation to each other. Addition of more S_1 will increase the mass of the solution a' without altering its composition, since it is a saturated solution at that temperature, but the mass of solid S_2 decreases by dissolving; finally all S_2 has dissolved, and the composition falls on $a'b'$ above a'. The solution is now unsaturated with respect to either solid, and grows richer in S_1 until the composition b' is reached, which is that of a solution saturated with S_1; from this point onward the composition of the liquid remains fixed while its quantity diminishes until the point b, representing pure solid S_1, is reached.

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[1] *Phil. Mag.*, (4) **49**, 1, 206, 266 (1875).

[2] *Ber.*, **20**, 2223 (1877).

[3] *Sitz.-Ber. Wien. Akad.*, **81**, II, 1058 (1880).

For an isoplethal study, we will assume a complex of S_1 containing a very small amount of S_2, as represented by c; this will serve not only to show all the phase changes possible, but will illustrate the very practical experiment of taking the melting point of a slightly impure solid. At c the complex consists of a mixture of two solids, S_2 being present only in traces, as the temperature rises along the isopleth c–d, no change occurs until the eutectic temperature, t_c, is reached. Here, liquid phase of the composition C is formed, and solid S_2 disappears in the formation of the solution; the relative amounts of solid S_1 and of solution are represented by the lengths $c'C$ and $c't_c$. Now, if our total composition were nearer that of C, the amount of the solution would be sufficient to be visible, and there would be a halt in the rise of temperature of the system while the endothermal formation of this solution was occurring; but, with the composition which we have purposely chosen, the amount of the liquid is so small that it is not visible, any more than would be a drop of water poured upon a bucket of sand, and there is no detectible halt in the temperature rise. As we now pass along $c'd'$ toward d', the length t_c–c' representing the relative mass of solution remains constant, while the length representing the mass of solid S_1 is constantly decreasing, which means that in reality we are obtaining more liquid phase and losing solid phase. At some point, e, the amount of liquid becomes large enough to be seen, and the total mass "softens"; from then onward it becomes softer and softer, until at d' it clarifies completely with the disappearance of solid. To speak in the inexact terms of the experiment, the solid did not melt sharply, but melted between the temperatures e and d'. It will be seen that the length of this temperature interval decreases as the isopleth is raised toward the axis S_1, so that the "sharpness" of the melting point is a criterion of the purity of S_1. Only in the complete absence of a second component does the substance possess a true melting point, R.

Systems of two components which are represented diagrammatically by Fig. 14 are very numerous. They include many pairs of organic compounds and of inorganic compounds; salts with water fall into this class in numerous instances, and the solubility curve of a salt as given in the various solubility tables is usually a section, more or less complete, of one of the curves of the diagram; metallic alloys occasionally fall into this class. The term alloy is so broadly used that it is not easily defined; most simply phrased, an alloy is a substance containing two or more components which are metals. In practice, however, we do not hesitate to apply the term to iron-carbon alloys, in which only one of the components is a metal. In Table XXIII are given three typical cases of systems which may be represented by Fig. 14.

TABLE XXIII

SOLUBILITY CURVES WITH EUTECTICS

Point	Cyclohexane: Benzene[1]		Silver Nitrate: Water[2]		Lead: Silver[3]	
	Temp.	Per Cent Cyclohexane	Temp.	Per Cent Silver Nitrate	Temp.	Per Cent Silver
M	+ 5°	0	0°	0	327°	0
	− 5.2	17.04				
	− 11.3	28.26				
	− 26.9	52.88				
	− 36.2	65.05				
C	− (44)	(75)	− 7	46.2	303.3	5
	− 37.1	78.55	+ 5	56.3	460	10
	− 31.2	84.56	20	67.8	535	20
	− 16.5	88.34	40.5	76.8	648	50
	− 6.7	93.42	135	92.8	875	85
R	+ 6.2	100	208	100	961.5	100

[1] Mascarelli and Pestalozzi, *Gazz. chim. ital.*, **38**, 38 (1908).

[2] Etard, *Ann. chim. phys.*, (7) **2**, 524 (1894).

[3] Petrenko, *Z. anorg. Chem.*, **53**, 200 (1907).

In the case of alloys, the conditions at the eutectic are of importance, not only as determining the lowest melting point for the metallic pair but also as affecting the structure and physical properties of the solid alloy. If some composition other than the eutectic composition be taken and the molten metallic solution cooled, upon reaching the freezing-point curve *RC* or *MC* in Fig. 14 (dependent on whether S_1 or S_2 is in excess), crystals of the one component begin to form throughout the liquid mass. When the temperature has dropped to the eutectic temperature, t_c, it will there remain constant and crystals of both S_1 and S_2 will form in the eutectic ratio and continue to form until the mass is entirely solid. This crystallization of the two solids in a continuously uniform ratio fills in the interstices between the crystals previously formed with a conglomerate which, though truly a mixture, is remarkably uniform in character. By the methods of metallography, such metallic surfaces can be examined under the microscope; under high magnification the eutectic mixture shows its heterogeneity, as in Fig. 15*a*, but its approximation to homogeneity as shown in Fig. 15*b* is such that in metallographic work it is looked upon as a "structural element" as if it were a single phase.

Ib. Pure Components as Solid Phases, with Two Liquid Phases Occurring: It has previously been pointed out that if a system of two conjugate liquids with an upper consolute temperature be cooled, and if it be the fact that no lower consolute point exists, a solid phase will eventually appear. There will then be present four phases ($S - L_1 - L_2 - V$) and the system is invariant. Such a system must show in its graph a two-liquid area in connection with a solubility curve such as was discussed in the preceding examples; Fig. 16 is a

PLATE III.

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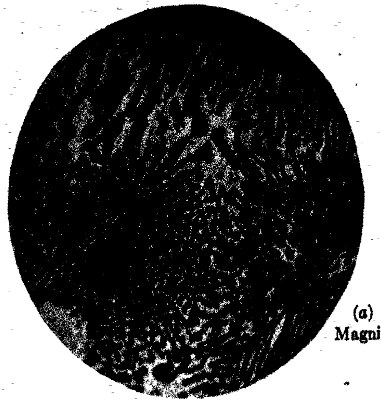

(a)
Magnified 500 times.

(b)
Magnified 150 times.

FIG. 15.

Ag-Cu ALLOY, SLIGHTLY TO THE Cu SIDE OF THE EUTECTIC POINT (73% Ag, 27% Cu).

Diagrams by courtesy of
Prof. D. P. Smith and Mr. J. L. Whitten.

type figure drawn to represent such relations, in which the points A and B represent the composition of the two conjugate liquids which are in equilibrium with the solid phase S_1 at the temperature t. It will be seen that such a system contains the two-liquid curve shown earlier in Fig. 11 and the two solubility curves shown in Fig. 14, the difference being in the apparent break in the solubility curve CB-AR (Fig. 16) at its points of contact with the two-liquid curve. The only new considerations that enter are, therefore, limited to this point in the diagram.

The temperature t at which these four phases are in equilibrium gives us an added example of a quadruple point. We have previously discussed the eutectic as such a point, the phases being $S_1 - S_2 - L - V$; the transition temperature of two polymorphic forms, mentioned previously but not discussed, is of the same class, with two solids, one liquid and vapor; our new example differs in having two coexisting liquids. No specific name has been given to this type of quadruple point, but it is nevertheless one of considerable interest. Its recognition gives us a phase-rule explanation of a common occurrence in organic practice, namely, the so-called "melting under water" of various compounds, this phenomenon occurs frequently at temperatures far below the true melting point of the pure compound. It will occur invariably in two-component systems of the type under discussion if one experiments with complexes of a composition intermediate between A and B, the two conjugate solutions; such a complex is represented by x in Fig. 16.

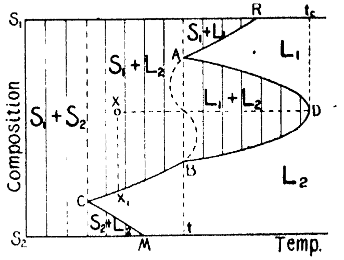

FIG. 16 The System $S_1 - S_2$. The Solid Phases are Pure Components with Two Liquid Phases Present

At the initial temperature of x, the system consists of the solid S_1 in equilibrium with its saturated solution x', as can be read from the diagram, if the temperature be raised along the isopleth xD, the concentration of the solution rises along CB, finally reaching the composition B. At the quadruple point t the temperature rise will halt, and as the solid S_1 continues to dissolve, a new liquid phase begins to form, of the composition A. It will be seen that the new liquid is *not* simply a layer of molten S_1, but is a solution, the phenomenon is then not at all the melting of a solid into a liquid of identical composition, as happens with a pure one-component body, but is the formation of a second conjugate liquid. On continued application of heat, the solid S_1 will disappear completely, and only two liquids (with vapor) remain; the continuation of the isopleth to the point D has been discussed in connection with Fig. 11.

This phenomenon of "melting under water," or indeed under any other liquid, since it represents an invariant temperature, is a perfectly definite property for any compound, and might serve as a criterion of its purity, although in practice other properties are more convenient. A few examples of such quadruple points follow.

TABLE XXIV

THE QUADRUPLE POINT $S - L_1 - L_2 - V$

Substances	M.P. of Pure Component	Quadruple Temp.	Wt. Per Cent of First-named Component	
			L_1	L_2
Benzoic acid-water	121.4°	98°	71	7
Phenol-water	42.7	1.7	72	2.5
Succinic nitrile-water	53	18.5	92	10.2
Water-ether	0	− 3.8	99	87.3
Resorcin-benzene	110	95.5	68.5	15

At invariant temperatures such as appear at t and t_c in Fig. 16 there occur phase reactions; that is, the addition or subtraction of heat results in the passage of substances from one phase to another, without change of temperature, and in the ultimate appearance or disappearance of a phase. The course of such phase reactions can be easily followed from the diagram.

At the temperature t, omitting reference to the vapor phase, which will be present after the reaction as well as before, the compositions of the three phases which bear a conjugate relation, as shown by the tie-line t, are represented by S_1, A and B. Of these, A (one of the solutions) is intermediate in composition between S_1 and B; it follows geometrically that A can be formed from certain quantities of S_1 and B, but that it is impossible to form S_1 alone from any quantities of A and B, or B alone from any quantities of A and S_1. The phase of intermediate composition is formed always from those of the extreme composition, and the phase reaction which occurs upon adding or subtracting heat is

$$S_1 + L_2 \rightleftarrows L_1,$$

where L_2 stands for the composition B and L_1 for the composition A.

It remains to decide which of these reversible changes occurs upon addition of heat and which upon subtraction. If thermal data are available, the conclusion could be reached by use of van't Hoff's law; but in the absence of such data, the diagram will give the answer. Inspection shows that areas in which L_1 is represented exist only at temperatures above t, while S_1 and L_2 exist both below and above that temperature; hence, the arrow pointing to the right represents the reaction resulting upon addition of heat. We may also deduce what univariant equilibria (two phases plus vapor) have their origin at this quadruple point. There will be as many as there are combinations of two out of the three phases, which are:

$S_1 + L_2$, at lower temperatures (curve BC),
$L_2 + L_1$, at higher temperature (curve BDA),
$L_1 + S_1$, at higher temperature (curve AR).

If now we apply the same reasoning to conditions at the other quadruple point, namely, the eutectic C, we obtain the following:

Phase reaction: $S_1 + S_2 \rightleftarrows L_2$

Univariant equilibria: $S_1 + S_2$, at lower temperatures,
$S_1 + L_2$, at higher temperatures (curve $CB - AR$, since L_1 and L_2 are equivalent when not conjugate),
$S_2 + L_2$, at higher temperatures (curve CM).

From the invariant points existing for the system, we have deduced all the univariant equilibria which exist (i.e., all the curves of Fig. 16). There remains for discussion only the question of the solubility curve for $S_1 + L$ between the points A and B. To this is ascribed an S form (shown in the dotted lines), with a point of inflection, such as is drawn to represent the van der Waals equation for $p - v$ relations of a gas and liquid, and such as has previously been shown in Fig. 10. Of course, all parts of this are either metastable or unrealizable.

As a complete example of a system represented by Fig. 16, the data for succinic nitrile and water are given in Table XXV.

TABLE XXV

SUCCINIC NITRILE AND WATER[1]

Solubility Curves			Conjugate Liquids: Curve BDA			
Temp.	Mol. Per Cent Nitrile	Point	Temp.	L_2 Mol. Per Cent	L_1 Mol. Per Cent	Point
0°	0	M	18.5°	2.5	72	B, A
− 1.2	1.29	C	20	2.7	70.7	
0	1.36		39	- -	56.4	
17	2.3		45	5.97	--	
18.5	2.5 and 72	B, A	53.5	10	30.7	
24	76.6		circa (55.5)	circa 20	20	D
29.3	81.2					
54.5	100	R				

[1] Schreinemakers, *Z. physik. Chem.*, **23**, 439 (1897).

As special cases falling into this class should be included systems in which the conjugate solutions are metastable, i.e., the curve ADB is wholly to the left of the solubility curve $CBAR$, as Alexejew found for salicylic acid and water,[2] and also the rare instances in which the conjugate solutions show a lower consolute temperature, in which case the conjugate curve is conjoined to a descending solubility curve; such a relation exists in the system: potassium iodide-sulphur dioxide.[3]

IIa. Compounds as Solid Phases, without Congruent Melting Points: Systems of this type introduce few considerations not already advanced. They are, however, extremely common; whenever any two components show a high degree of solubility, it is probable that there is more or less compound formation in the liquid phase, and frequently one or more of these compounds will form solid phases as well; the formation of solid hydrates of salts for example is of the commonest occurrence. The classical instance of a system of this type is given by sodium sulfate and water; studied first more than a century ago by Zis and by Gay-Lussac,[1] it has had its various solubility curves and transition points determined by a number of investigators, the work having been completed recently by Wuite[2] at the high temperatures leading up to the critical temperature of the solution. The composition-temperature diagram is shown schematically in Fig. 17. The curve *AB* is the freezing-point curve

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[2] *Wied. Ann.*, **28**, 305 (1886).

[3] Walden and Centnerszwer, *Z. physik. Chem.*, **42**, 432 (1903).

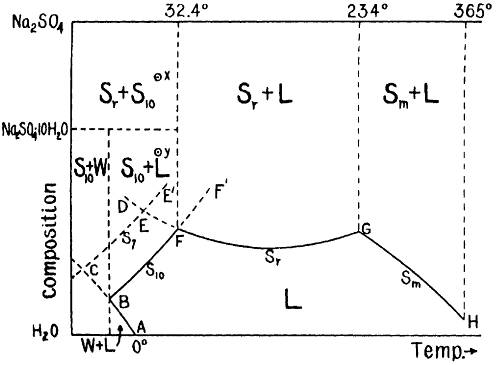

FIG. 17. *t.-c.* Diagram for the System, Sodium Sulfate-Water

for ice, which ends at the eutectic *B* (– 1.2°); here the other solid phase is the decahydrate, $Na_2SO_4.10H_2O$, which is an additive compound formed of the two components. The solubility curve for the decahydrate rises with the temperature up to 32.4°, which is its transition temperature (F.) to the anhydrous form and the distinctive point of this diagram. The curve for the anhydrous sulfate shows a solubility diminishing with rise of temperature up to about 125° where it reaches a minimum value, afterward rising until the temperature is 234°. Here (point *G*) occurs a transition from the common crystalline form, which is rhombic, to a polymorphic monoclinic form which has a diminishing solubility up to 365°, which is the critical temperature of the solution; the concentration of the salt in the liquid phase is here very low and the critical temperature is practically that of pure water. The four solid phases occurring in equilibrium with solution along this curve are represented by *W* (ice), S_{10} (decahydrate), S_r (rhombic anhydrous salt) and S_m (monoclinic anhydrous form). The data for these four solubility curves follow, the composition of the solution being given, as is customary, in weight per cent of Na_2SO_4 present, irrespective of the nature of the solid phase.

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[1] Zis, *Schweigg. Journ.*, **15**, 160 (1815). Gay-Lussac, *Ann. chim. phys.*, **11**, 296 (1819).

[2] *Z. physik. Chem.*, **86**, 349 (1914).

TABLE XXV-A

THE SYSTEM: SODIUM SULFATE-WATER

Solid Phase: Ice (*AB*)[1]		Solid Phase. $NaSO_4\ 10H_2O$ (*BF*)[2]		Solid Phase: Na_2SO_4 Rhombic (*FG*)[3]	
Temp.	Per Cent Na_2SO_4 in Solution	Temp.	Per Cent Na_2SO_4 in Solution	Temp.	Per Cent Na_2SO_4 in Solution
– 0.6°	1.96	0°	4.76	35°	33.4
– 1.2	3.85	10	8.3	50	31.8
		20	16.3	100	29.8
		30	29.0	190	30.4
		32.7	33.6	234	31.0

Solid Phase: Na_2SO_4 Monoclinic (*GH*)[3]		Solid Phase: $Na_2SO_4\ 7H_2O$ (*CE*)[2]	
Temp.	Per Cent Na_2SO_4 in Solution	Temp.	Per Cent Na_2SO_4 in Solution
250°	29.5	0°	16.3
279	25.3	5	19.4
319	17.2	10	23.1
		15	27.0
		20	30.6
		25	34.6

[1] de Coppet, *Ann. chim. phys.*, (4) **25**, 539 (1872), *Z. physik. Chem.*, **22**, 239 (1897).

[2] Seidell, Solubilities, N. Y., 1919, p. 667.

[3] Wuite, *loc. cit.*

This system shows the phenomenon of suspended transformation to a marked extent, as indicated by the dotted lines in the diagram.

The solubility curve for the decahydrate *BF* has been carried some distance beyond the transition temperature of 32.4°, to the point *F′*. Here, as in all cases of solubility, the solubility of the metastable body is higher than that of the stable body, so that if a crystal of the anhydrous salt is put into the solution of the composition *F′*, the solubility drops to *F* with a simultaneous drop of temperature, since the precipitation of the solid is an endothermic reaction. The solubility curve of the rhombic anhydrous salt, *GF*, has also been prolonged a considerable distance into the metastable region, as shown by *FD*, and the ice curve *AB* has been extended to *C*. In this metastable region to the left of *BF* a second hydrate, of the formula $Na_2SO_4\ 7H_2O$, has been found, having a solubility curve *CE*, it is itself metastable and gives rise to a metastable eutectic with ice at – 3.55° (*C*) and a metastable transition point to the decahydrate, *E*, at 24.2°. The data for this curve are given as the last part of Table XXV.

The complete system, $Na_2SO_4 - H_2O$, shows the five quadruple points or invariant points *B*, *C*, *E*, *F* and *G*. *B* and *C* will be recognized at once as eutectics. E, F and G are transition points, of which we will discuss one (F) in some detail. The point F represents the stable transition point of the decahydrate to the rhombic anhydrous form, the phase reaction being the following: $Na_2SO_4 . 10H_2O \rightleftharpoons Na_2SO_4 +$ solution. The change from left to right represents a partial fusion, since the solid hydrate changes to a solution plus a second solid; such a transition is sometimes called an *incongruent melting point*, to distinguish it from a true or congruent melting point, which will be discussed with our next type of system. While not a melting point in the exact sense, it is nevertheless a change of great practical usefulness, since it occurs at an invariant temperature and therefore gives a convenient means of obtaining a definite and constant temperature. If a sample of the hydrate be subjected to the influence of a higher temperature, it will maintain this constant temperature F until the transformation is complete. Richards[1] has found the temperature to be 32.383°, as carried out in an open vessel; this is not exactly the quadruple point, which by definition must be under the natural vapor pressure of the system, and has been found to be 32.6°.[2] The transition points of this and other hydrates give us one of our most convenient methods of obtaining fixed points for the standardization of thermometers.[3] Such transition points are also of use in making constant-temperature baths for experimental work. Further, since the transition from anhydrous salt to hydrate is an exothermic change, such materials find use as thermophores or heat-producing mixtures for warming purposes; thus, a quantity of sodium acetate and water, if heated above its transition point and allowed to cool, forms a metastable saturated solution of the anhydrous salt and water, but, upon crystallization of the stable hydrate being started by agitation or other means, the temperature will rise to the transition temperature (58°)[4] of the compound $NaC_2H_3O_2 \, 3H_2O$ and remain at that temperature until all the heat of transformation has been evolved.

We shall consider next the vapor-pressure relations of this system. In the first place, it should be stated that for a two-component system there can be no such thing as the vapor pressure of a single solid such as $Na_2SO_4 . 10H_2O$, for if we imagine a vessel containing only this solid and water vapor there are but two phases present, so that the system is bivariant and any vapor pressure may be maintained within certain limits. It is only when three phases are present that the system becomes univariant and has a definite vapor pressure for each temperature, and this vapor pressure will depend upon which choice of three phases is present. We must consider then the vapor pressures of all the various phase-complexes, and not the indefinite pressures of a single compound or solution. The three-phase univariant systems with the two components sodium sulfate and water (omitting the heptahydrate from consideration because of its metastability, and the monoclinic anhydrous form because of the high temperatures required) are the following, vapor phase being assumed present in each instance: $S_r - L - V$, $S_{10} - S_r - V$, and $S_{10} - L - V$. In Fig. 18 these three curves are shown schematically; the solution phase is in each case the saturated solution, since only when saturated can it remain in equilibrium with the solid phase. The continuous curve *AB* is the curve for the pressure of the system consisting of rhombic anhydrous salt and saturated solution; it rises with temperature rise, and is here shown for temperatures both below and above its transition point *C* at 32.4°. Considering next the curve for the decahydrate and saturated solution, it must, at the lower temperatures where it is in stable equilibrium, have a higher vapor pressure than the first system, since the concentration of salt in its saturated solution is less than in the metastable solution; we must represent it therefore by a point *D*, above *A*. This curve also will rise with rising temperature and must pass through the point *C*, since at that temperature the same solution is saturated with respect to both solid phases; the two systems could not have different vapor pressures, otherwise, vapor would distill from one to the other, or, in other words, the two systems would not be in equilibrium. The curve *DC* therefore lies above *AC* throughout; and it should be pointed out that there is no inconsistency in the stable system having the higher vapor pressure, but that, for a two-component system where solutions are present, the higher vapor pressure for the stable system is a necessity. The third system, consisting of the two solid phases and vapor, has the lowest vapor pressure, which is represented by *EC*; it is a stable system below 32.4°, for certain ranges of composition as shown in the upper left-hand corner of Fig. 17. This curve also must pass through the quadruple point *C*, since at that temperature the two solids are not only in equilibrium with each other but are also in equilibrium with solution, and hence must show the same vapor pressure as systems including the solution. The complete diagram shows one three-phase system stable above 32.4° and two systems stable below; above that temperature there is therefore only one equilibrium vapor pressure possible for three phases, while below it there may be either of two. Which of these two will prevail at a given temperature is solely a question of the total quantities present in the system. Let us suppose that, in a desiccator at room temperature, is put a large quantity of anhydrous Na_2SO_4 as a drying agent and above it a dish containing a small amount of saturated solution including crystals of $Na_2SO_4 . 10H_2O$; in that case the total composition will be represented by the point *x* in Fig. 17. The vapor pressure

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[1] Richards, *Z. physik. Chem.*, **26**, 690 (1898); Richards and Wells, *ibid.*, **43**, 465 (1903); Dickinson and Mueller, *J. Am. Chem. Soc.*, **29**, 1381 (1907).

[2] Cohen, *Z. physik. Chem.*, **14**, 90 (1894).

[3] Richards, *loc. cit.;* Richards and Churchill, *ibid.*, **28**, 313 (1899); Richards and Wells, *loc. cit.;* Richards and Wrede, *ibid.*, **61**, 313 (1908); Richards and Fiske, *J. Am. Chem. Soc.*, **36**, 485 (1914).

[4] The transition point is very close to the metastable conjugate melting point; Green, *J. Phys. Chem.*, **12**, 655 (1908); Miller, *ibid.*, **12**, 649 (1908).

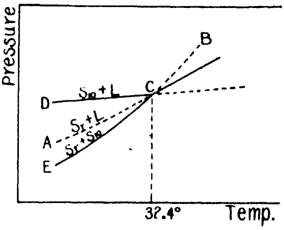

Fig. 18 *p-t* Diagram for the System, Sodium Sulfate-Water (Schematic) of the system $S_{10} + L$ (*DC* in Fig. 18) is higher than that of $S_{10} + S_r$ (*EC* in Fig. 18); vapor at the higher pressure will therefore hydrate the anhydrous desiccating agent, forming the system of lower vapor pressure, and the solution will evaporate completely, leaving pure $Na_2SO_4.10H_2O$ on the dish under a pressure on the line *EC* (Fig. 18). Such a system can be used to obtain a hydrate of definite composition for analytical purposes.[1] If, on the other hand, the amount of anhydrous Na_2SO_4 taken were small, so that the total composition is that of *y* in Fig. 17, it would be completely hydrated before the solution is evaporated, and the higher vapor pressure represented by *DC* (Fig. 18) would prevail.

IIb. Compounds as Solid Phases, with Congruent Melting Point: In a large number of systems in which additive compounds exist, it is found that these compounds not only possess a transition point such as has been described above, but also possess the property of melting sharply and distinctly into a liquid of the same composition as the solid. Such bodies are said to possess a *congruent melting point,* and possess a solubility curve quite different from those previously discussed. Phenol and aniline fall into this class, and will serve as our example. In this system three different solid phases appear, namely, aniline, phenol, and a compound of the formula $C_6H_5NH_2.C_6H_5OH$. These give rise to three solubility curves which are represented in Fig. 19 by the three curves *de*, *ab*, and *bcd*; the data follow from which the curves are drawn.

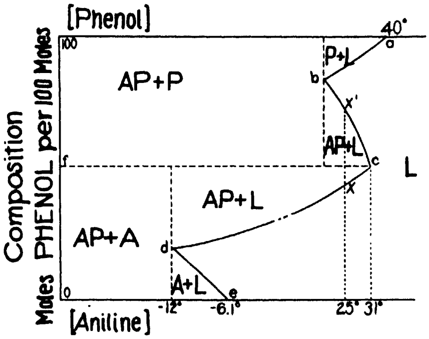

FIG. 19. The System, Phenol-Aniline (Schematic)

The composition of the solutions is given in molar percentages, which is always the most logical method of representing composition and is here of especial convenience where the composition of compounds is to be deduced. The point *d* in Fig. 19 is a eutectic, from which originates the solubility curve for the compound, *dc*; the solubility increases with temperature up to 31° and

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[1] Hill and Smith, *J. Am. Chem. Soc.*, **44**, 546 (1922).

TABLE XXVI

THE SYSTEM: ANILINE-PHENOL[1]

Aniline in Solution in Moles per 100 Moles

Solid Phase: Aniline (*de*)		Solid Phase. Compound (*bcd*)		Solid Phase Phenol (*ab*)	
Temp.	Composition	Temp.	Composition	Temp.	Composition
− 6.1°	100 *e*	(− 12°)	( ) *d*	(15°)	( ) *b*
− 7.1	98.5	− 5.2	89.2	18.5	20.4
− 8.1	96.9	+ 5.7	83.7	25.3	15.4
− 9.5	94.8	22	70.1	29.5	11.6
− 11.4	92.4	27.5	60.9	32	9.8
− (12)	( ) *d*	29.5	55.5	35	6.5
		(31)	(50.0) *c*	37.3	4.0
		29.9	45.2	(40)	0.0 *a*
		27.7	37.3		
		24.9	33.3		
		18	25.4		
		16.2	23.4		
		(15)	( ) *b*		

[1] Schreinemakers, *Z. physik. Chem.*, 29, 581 (1899).

a composition of 50 per cent molar of aniline and of phenol, that is, a 1 : 1 molar ratio. This is, from the diagram, the point of maximum temperature at which the compound can exist in equilibrium with solution, the solution, it will be seen, has here the same composition as the solid. This point, invariant in that there are present three phases and that the restriction is imposed that solution and solid shall have the same composition, is the congruent melting point: it is also spoken of as a *dystectic*, in contradistinction to a eutectic, it being the highest melting point and the eutectic the lowest. From *c* the curve is retrograde to the point *b*, which is a second eutectic with compound and phenol as the two solid phases.

A curve of this character, showing a maximum temperature and a retrograde direction upon one branch, is considered proof of both the occurrence and the composition of a compound;[2] the composition is read directly from the ordinate (here 1 : 1 of phenol and aniline) and is therefore known without the necessity for the isolation and analysis of the solid. In many cases the separation of a solid for analysis is difficult or impossible, in such cases the phase-rule evidence is invaluable. Our knowledge of compound formation in alloys, for example, is very largely based upon evidence of this type.

It will be at once observed that, at certain temperatures, such as 25° in the above case, there are two solutions, x and x' respectively, which can be in equilibrium with the same solid phase (here the compound, abbreviated as *AP*) at the same temperature. This paradox finds a simple explanation if we look upon our diagram as showing two systems and divided along the line *fc*; con-

[2] An exception to this reasoning is the occurrence of a maximum freezing point of a *solid solution*, which will be discussed later.

sidering now the upper half, it shows the two-component system, phenol-compound, with a perfectly regular pair of freezing-point curves such as were given earlier in Fig. 14. The choice of these two components is entirely permissible, since the composition of all the phases may be expressed in terms of the two; and the freezing-point curve of the compound (*cb*) shows the usual depression of freezing point with addition of the second component, phenol. In like fashion the lower half of Fig. 19 represents the system aniline-compound, and the freezing point of the compound is lowered by the addition of aniline. Returning to the complete figure, the freezing point of the compound is lowered by either aniline or phenol, as it would be with any component, whether or not that component could enter into its own composition. Any system showing congruent melting points may be resolved, for purposes of interpretation, into a number of two-component systems along the lines of the composition of the congruently melting compounds.

In the study of systems composed of a salt and water, many examples of hydrates are found which melt congruently and have diagrams built upon the type of Fig. 19. Thus, to mention a few, the hydrate $Na_2S_2O_7.5H_2O$ melts congruently at 56°, and $NaC_2H_3O_2.3H_2O$ at 58°; calcium chloride forms the hydrates $CaCl_2.6H_2O$, $CaCl_2\ 4H_2O$ (alpha form), $CaCl_2\ 4H_2O$ (beta form), $CaCl_2.2H_2O$ and $CaCl_2.H_2O$, of which only the hexahydrate[1] melts congruently. The system ferric chloride-water[2] is perhaps the most striking instance of multiple congruent melting points. There are four stable hydrates, $Fe_2Cl_6.12H_2O$,[3] $Fe_2Cl_6.7H_2O$, $Fe_2Cl_6\ 5H_2O$ and $Fe_2Cl_6.4H_2O$, all possessing congruent melting points. The detailed solubility data will be omitted, but the temperatures and compositions at the six eutectics and the four congruent melting points are given below. Fig. 20 represents the system graphically.

TABLE XXVII

THE SYSTEM: FERRIC CHLORIDE-WATER

Point (Fig. 20)		Temperature	Solid Phases	Moles Fe_2Cl_6 per 100 Moles H_2O
M.P. . . .	*A*	0°	Ice	0
Eutectic . . .	*B*	− 55	Ice : $Fe_2Cl_6\ 12H_2O$	2.75
Dystectic. . .	*C*	+ 37	$Fe_2Cl_6.12H_2O$	8.33 (= 1 : 12)
Eutectic . .	*D*	27.4	$Fe_2Cl_6\ 12H_2O$: $Fe_2Cl_6\ 7H_2O$	12.15
Dystectic. . . .	*E*	32.5	$Fe_2Cl_6.7H_2O$	14.29 (= 1 : 7)
Eutectic.	*F*	30	$Fe_2Cl_6.7H_2O$: $Fe_2Cl_6\ 5H_2O$	15.12
Dystectic. . . .	*G*	56	$Fe_2Cl_6.5H_2O$	20.00 (= 1 : 5)
Eutectic. . . .	*H*	55	$Fe_2Cl_6.5H_2O$: $Fe_2Cl_6\ 4H_2O$	20.32
Dystectic . . .	*J*	73.5	$Fe_2Cl_6.4H_2O$	25.00 (= 1 : 4)
Eutectic. . . .	*K*	66	$FeCl_6.4H_2O$: Fe_2Cl_6	29.2
Eutectic.	*M* (metastable)	15	$FeCl_6.12H_2O$: $Fe_2Cl_6\ 5H_2O$	

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[1] Roozeboom, *Z. physik. Chem.*, **4**, 31 (1889).

[2] Roozeboom, *ibid.*, **10**, 477 (1892).

[3] The double formula Fe_2Cl_6 is used in order to avoid fractional coefficients for the water

In systems like the above, in which only one of the components is appreciably volatile (here the water), very interesting phase changes occur upon isothermal evaporation. Let us assume that an unsaturated solution of ferric chloride and water be maintained at a constant temperature of 31°; the point is represented by x in Fig. 21. If it be allowed to evaporate at this temperature, all changes that occur will be represented by the intersection of the isotherm at 31° with the various solubility curves. As water evaporates, the solution becomes more concentrated, until at the composition 1 it begins to precipitate $Fe_2Cl_6\ 12H_2O$. The composition of the solution, which is now saturated, of course remains constant until it has completely evaporated, leaving only solid behind; meantime, the total composition has risen to the point 2, which is the composition of the hydrate. As water now leaves the hydrate by evaporation, solution of the composition 3 begins to appear, increasing in amount until the whole mass has liquefied and has the composition of the point 3; that is, by removal of water isothermally, the solution x has first changed completely to solid and then changed completely to liquid. Following the isotherm upward, at the points 4, 5 and 6 the process is again repeated in detail, and at 7 there is a third solidification which is not again followed by liquefaction. These remarkable changes, which find simple representation in a phase-rule diagram, would be quite inexplicable in the absence of the phase rule.

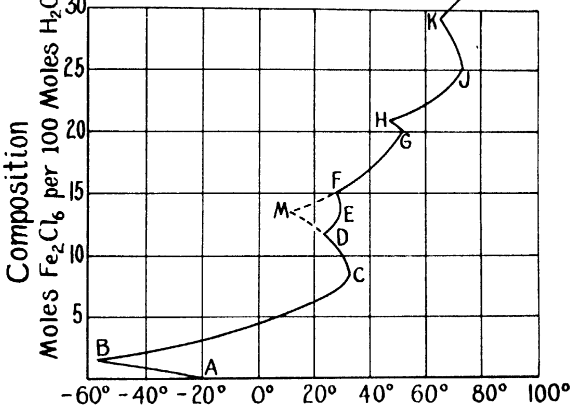

FIG. 20. The System, Ferric Chloride-Water (Schematic)

General Considerations Relative to Types Ia, Ib, IIa and IIb: Solubility curves such as those of type IIb, in which congruent melting points occur, have been shown to be of great value in determining the existence and composition of compounds. Such curves, for example, will determine beyond dispute in the case of optical isomers whether the inactive form is a racemic mixture or a racemic compound; in the first instance the freezing-point curves,

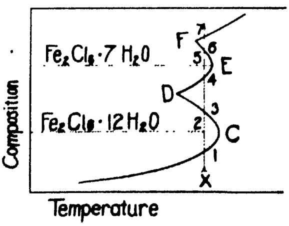

FIG. 21. Isothermal Evaporation in the System, Ferric Chloride-Water

or solubility diagram, will show a single eutectic only (as in Fig. 14), while in the latter case there will be two eutectics and a congruent melting point (as in Fig. 19). In this latter case the diagram will show perfect symmetry; inasmuch as optical antipodes show similar physical properties, the two melting points of the pure components will be the same, the slope of the two solubility curves will be the same, and, as a result, the two eutectics will have the same temperature; and the composition ratio at one of them will be simply the inverse of that at the other. The congruent melting point may be either higher or lower than the melting point of the pure components.

It will be apparent that systems may show the types of curves indicated for more than one type; thus calcium chloride and water show points of incongruent transition as well as congruent melting points, and the formation of two liquid phases is by no means restricted to systems showing only a single eutectic, like succinic nitrile and water (Fig. 16), but occurs as well where there are transition points and congruent melting points. However, any two-component system (excepting those in which solid solution occurs, which still remain to be discussed) can be treated as a combination of these four types; in short, solubility curves, transition points, eutectics, congruent melting points and melting points of components include all the phase relations affecting the solid-liquid equilibrium.

Eutectics for the system composed of salt and water have proven so useful for experimental work that an abbreviated list is given in Table XXVIII. Herewith are included, also, those for a few acids with water, and bases with water.

TABLE XXVIII

Two-Component Eutectics

Component	Solid Phase, with Ice	Eutectic Temperature	Wt. Per Cent Component
Na_2SO_4	$Na_2SO_4\ 10H_2O$	− 1.2°	3.85
$MgSO_4$.	$MgSO_4\ 7H_2O$	− 3.9	19
KBr	KBr	− 13	32.15
NH_4NO_3.	NH_4NO_3	− 17.35	41.2
NaCl.	NaCl	− 22.4	23
NaCl.	$NaCl\ 2H_2O$	− 21.2	22.4
$C_2H_4O_2$.	$C_2H_4O_2$	− 26.75	58.9
$CaCl_2$.	$CaCl_2\ 6H_2O$	− 55	29.9
$FeCl_3$.	$FeCl_3\ 6H_2O$	− 55	33.1
$AgClO_4$.	$AgClO_4\ H_2O$	− 58	73
KOH.	$KOH\ 4H_2O$	(− 70)	(32)
H_2SO_4.	$H_2SO_4\ 4H_2O$	− 75	38
HCl.	$HCl\ 3H_2O$	− 86	24.8

IIIa. Solid Solutions as Solid Phases; A Single Solid Solution Present: Abnormalities in the freezing-point curves of certain systems led van't Hoff[1] to the view that the solid being precipitated was not a pure component, but a solid phase of variable composition to which he gave the name *solid solution.* Brief reference to solid solution has been made in the section on the Distribu-

[1] *Z. physik. Chem.*, 5, 322 (1890).

tion Law. A definition of such a substance is simple; it is to be viewed as a phase and therefore homogeneous, and of variable composition and therefore a solution, existing in the solid state. The concept of a solid solution occasionally gives difficulty, but if approached *de novo* it is no more difficult (and also no less difficult) than the concept of a liquid solution. It is the idea of homogeneity in a body in which we know that there is more than one substance present that gives the difficulty; and it is true that to admit salt water as homogeneous is perhaps impossible philosophically and no less so if one prefers to think in terms of the molecular hypothesis. But salt water is homogeneous if defined empirically; that is, heterogeneity has not been demonstrated experimentally, and the treatment of it as homogeneous under the phase rule brings about no contradictions. In exactly the same manner, a solid solution is regarded as homogeneous for the same empirical reasons. The difficulty to the student has not been lessened by calling these solid solutions by the contradictory name of "mixed crystals," when the essential fact is that a solid solution is *not* a mixture of crystals, but a uniform, homogeneous phase.

In solid solution the condition is independent of the state of the pure components under the same temperature and pressure, just as for liquid solutions; that is, the phase is equally a solid and equally homogeneous whether it be made from a solid and a gas, a solid and a liquid, or from two solids. The property of solubility in the solid state is however much less common than in the liquid state, as has been previously pointed out, and of course less common than in the gaseous state, where all components are soluble.

In dealing with liquid solutions, we have learned that, in some two-component systems, the liquids show complete mutual solubility, giving rise to but a single liquid phase, while other systems, in which there is limited solubility, form two liquid phases bearing conjugate relation to each other. The same conditions prevail for solids; the two components may dissolve mutually in all proportions, forming only a single solid solution, or may possess limited solubility and form two solid solutions which are conjugate. Extending our use of the term conjugate beyond its application to two liquid solutions, it will be seen that we may have the conjugate relation between a liquid and a solid solution and also between two solid solutions. We shall give our attention first to cases where the conjugate phases are a liquid solution and a solid solution.

Our problem being to trace the course of the equilibrium between a solid (albeit a solid solution) and a liquid phase, it is obvious that, to show the changes of concentration with the temperature, a freezing-point curve can be constructed. In our previous attention to freezing-

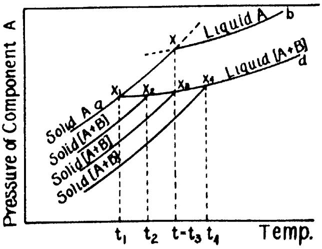

FIG. 22. Vapor Pressure of Component *A* in Solid and Liquid Phases

point curves we have assumed, in accordance with the laws of dilute solution, that the freezing point of a solid is always lowered by the presence of a second component in the liquid phase. This assumption is justified, by the laws of thermodynamics, as long as the solid phase is a pure component; but there is no foundation for any such generalization when the solid phase is a solid solution. In this case, the freezing point of the solid solution may be either lower than that of the pure component, equal to it or higher, and all three possibilities are known. Fig. 22 is designed to demonstrate qualitatively these three conditions.

Let us consider the vapor pressure of the component A alone (i.e., its so-called partial pressure) in a system composed of A and B. The curve ax is the vapor-pressure curve of the pure solid and bx that of the pure liquid phase, the two intersecting at x; this relationship for a single component has previously been shown in Fig. 4. Let us now consider that the liquid phase has an amount of B added to it; the curve representing the vapor pressure of A in this solution must fall below the curve for pure liquid A, since the vapor pressure of A is always lowered by a second component. The curve for this solution, dx_1, intersects ax at the point x_1, and the point of intersection is the freezing point, at which the vapor pressure of A in the two phases is the same, that being a necessary condition for equilibrium. The point x_1 is, by the diagram, necessarily at a temperature t_1 lower than t, which accords with the rule that where the solid phase is the pure component its freezing point is always lowered by a second component in the solution. Let us now consider however that the solid phase which forms is a solid solution containing varying quantities of B; the curves representing the pressure of A in these solid solutions fall below ax a distance dependent on the amount of B present in the solid phase. The intersections of these curves for the solid phase with that for the liquid phase (dx_1) are the freezing points, where the pressure of A in both phases is the same; and it will be seen that, according as the solid phase contains little or much B, the freezing point is below $t(t_2)$, equal to it (t_3) or above it (t_4). As to the concentrations in the phases at these various points, it can be shown thermodynamically, as it has been shown experimentally, that the following rule holds; if the concentration of the second component is greater in the liquid phase than in the solid phase, the freezing point is lowered (x_1 and x_2), and if it is greater in the solid phase, the freezing point is raised (x_4).

What has been shown for solid solutions in which A is the predominating component may also be shown where B predominates; it follows then that in a general system $A - B$ where solid solution occurs, the freezing point of each solid phase may be lowered, the freezing points of each may be raised, or one may have its freezing point raised and the other have it lowered.[1] There will therefore be three types of curves necessary to express these three cases.

Let us now recapitulate what has been learned about systems consisting of a liquid phase and single solid solution, so that we may be in position to interpret complete diagrams: (1) there will be a liquid solution and solid solution bearing a conjugate relation to each other, and of course two separate curves will be necessary to show the composition of these two phases; (2) since only one solid phase and one liquid phase have been postulated, and only one vapor phase is possible, there can not be more than three phases present, and no invariant points, which require four phases (eutectics, transition points, etc.), can appear;

[1] The special case in which freezing points are neither raised nor lowered will not be discussed in detail; the two optically active oximes of camphor offer an example of this case.

(3) the freezing points of a pure component may be either raised or lowered by the second component, giving rise to three types of curves.

In Fig. 23 have been drawn schematic representations of complete systems fulfilling these requirements. Curve I illustrates the case where each component has its melting point lowered by the second. The curve *agcfe* represents the composition of the liquid phase, and is called the *liquidus curve;* the dotted line *abcde* is the curve for the solid phase, called the *solidus curve*, and the tie-lines show the conjugate relation. The position of these two curves with reference to each other fulfills the rule developed above; at a given temperature *t* the liquid phase *f* contains more of *A* than does the solid phase *d* which therefore has a lower melting point than that of pure *B*(*e*), and likewise the liquid *g* contains more of *B* than does the solid phase *b*, in accordance with which its melting point is lower than that of pure *A*(*a*). The point *c* bears a superficial resemblance to a eutectic, but is in no sense to be regarded as such, since it is not an invariant point; it is correctly described as a minimum melting point, which is a characteristic point in systems of the type in which each component has its melting point lowered by the other.

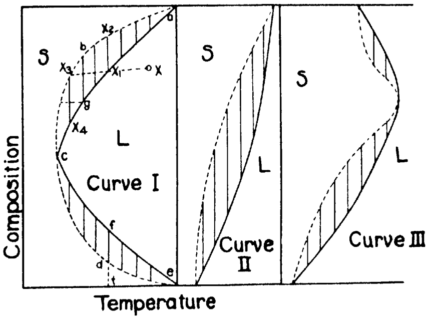

FIG. 23. The System A-B, Solid Phase, a Single Solid Solution

Information as to the melting and freezing points in such a system can be gained by following an isopleth from the point x toward lower temperatures. Starting with this composition and temperature, the mass is liquid until the temperature of x_1 is reached; here solid appears, but of the composition x_2, as indicated on the tie-line $x_1 - x_2$, and it is apparent that the solid will be relatively rich in *A* and the liquid rich in *B*. If now the temperature be allowed to fall, the isopleth crosses tie-lines joining all compositions of solid from x_2 to x_3, and all compositions of liquid from x_1 to x_4, the solid will therefore be increasing in amount and in concentration of *B* along the line $x_2 - x_3$ and the liquid decreasing in amount and also increasing in concentration of *B* along $x_1 - x_4$, so that the last drop of liquid has the composition x_4 and the total solid the composition x_3. If the temperature be halted between x_1 and x_3, fractional crystallization can be effected, this will be discussed later. The temperature x_1 is the temperature at which, for this composition, solid first appears, and is spoken of as the freezing point of that complex; by extension, the whole liquidus curve is regarded as a freezing-point curve. On the other hand, the point x_3 is the point at which liquid first appears on rising temperature, and is called the melting point, so that the solidus curve is a melting-point curve. For such a system it is clear that the terms melting point and freezing point represent entirely different temperatures; it is only where a solid liquefies to form a liquid phase of the same composition as itself that the term melting point and freezing point are interchangeable, as in the case of a one-component body or a compound melting congruently.

Mercuric bromide and iodide give curves represented by Curve I, Fig. 23, with a minimum point at 59 per cent $HgBr_2$ (molar) and 216.1°. The small inconsistencies at 100 per cent $HgBr_2$ and 0 per cent $HgBr_2$, as well as at the minimum point, represent experimental error.

TABLE XXIX

THE SYSTEM: MERCURIC BROMIDE-MERCURIC IODIDE[1]

Molar Per Cent $HgBr_2$	Freezing Point (Liquidus Curve)	Melting Point (Solidus Curve)
100	236.5°	236°
90	228.8	226
80	222.2	219
70	217.8	217
60	216.1	215.5
50	217.3	216
40	221.1	218
30	227.8	223
20	236.2	231
10	245.5	242
0	255.4	254

[1] Reinders, *Z. physik. Chem.*, **32**, 494 (1900).

The other two types of curves obtained are shown in Fig. 23 as Curves II and III. Curve II represents the case where the melting point of *A* is depressed by *B*, but that of *B* raised by *A*; hence the liquid phase at all temperatures is richer in *B* than is the solid phase, to account for melting points lower than that of *A*, or to state the same condition differently, the solid phase is richer in *A* than is the liquid phase, to account for melting points higher than *B*. Curve III represents the elevation of the melting points of both components, leading to a maximum melting point; the position of the liquidus and solidus curves will be found to accord with the rule relating to concentrations in the two phases with the rise in freezing point. Instances illustrating Curves II and III are known. In general, complete mutual solubility of the solids leading to systems represented by these three curves are not very common, and naturally enough occur most frequently where the two components are closely related, as benzene and thiophene (Table IX), mercuric iodide and bromide (Table XXIX), metals of like character or optical isomers.

IIIb. Solid Solutions as Solid Phases; Two Solid Solutions Present: When the two components show a limited solubility in the solid phase, a number of new relations appear. In the first place, these two solid solutions will bear a conjugate relation to each other. Secondly, if the temperature limits of this conjugate curve extend up to the temperatures where liquids exist, there will be two solids and a liquid coexisting which, with the vapor phase, make four phases and give rise to an invariant point which meets the definition of a eutectic or transition point. Further, either of these solid solutions alone may be in conjugate relation to the liquid phase giving rise to conjugate solidus-liquidus curves such as have been shown in Fig. 23. The conjugate relationship of the two solid phases will be discussed under a later heading, the relationships with the liquid phase being our present topic.

When the solidus-liquidus curves show a minimum melting point, like that of Fig. 23, Curve I, the existence of two solid solutions produces a eutectic at this point; the condition is shown in Fig. 24. Here the liquid of minimum freezing point, *b*, is in equilibrium with the two solid solutions of composition *d* and *e*, as shown by the tie-line *dbe*. This corresponds to a eutectic. Indeed, the system may be compared with the simplest melting-point diagram, that of Fig. 14, and the single distinction is that the liquid phases in Fig. 24 are conjugate with solid solutions, represented by *aef* and *cdg*, whereas in Fig. 14 they are conjugate with the pure components. Potassium nitrate and thallium nitrate [1] are an example of this class.

When the solidus-liquidus curves rise from the melting point of one component to that of the second, the system may be represented by Fig. 25. Here the juncture of the conjugate curve for the solid solutions (*fe* – *gb*) with the conjugate solid-liquid curves (*ad* – *ae*) produces an invariant condition where the phases are the two solid solutions *e* and *b*, the liquid solution *d* and vapor. This corresponds to a transition point, as shown earlier in Fig. 17, it is marked by the appearance of a new solid phase, whether one cools the system $S_1 + L$ or warms the system $S_2 + L_1$, and by a discontinuity of the solubility curve at *d*. Silver nitrate and sodium nitrate [2] offer an illustration of this type of

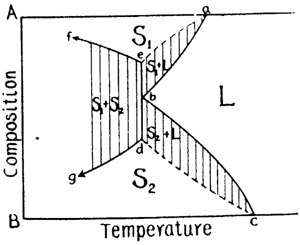

FIG. 24. The System A-B, Solid Phases, Two Solid Solutions with Eutectic

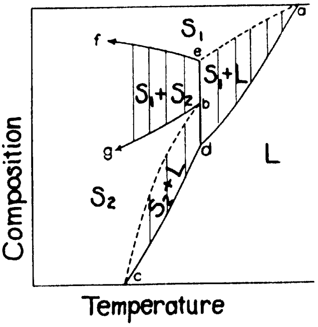

FIG. 25 The System A-B; Solid Phases, Two Solid Solutions with Transition Point

curve; the transition temperature t is 217.5°, at which temperature the liquid d contains 19.5 per cent molar of sodium nitrate, and the solid solutions b and e 26 per cent and 38 per cent respectively.

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[1] Van Eyk, *Z. physik. Chem.*, **30**, 430 (1899).

[2] Hissink, *Z. physik. Chem.*, **32**, 542 (1900).

General Considerations on the Solid-Liquid Equilibrium: The various systems that have been illustrated in the study of solid-liquid equilibrium require as experimental data a solubility curve in every case; that is, knowledge of the composition of the liquid phase at each temperature and likewise knowledge of the composition of the solid phase in equilibrium with it. The experimental methods for determining the composition of the liquid may again be classed as plethostatic and thermostatic. Among plethostatic methods the most commonly used is the so-called freezing-point method of Beckmann, which needs no description here; by it the temperature is determined at which solid phase begins to appear from a liquid complex of known composition. Similar in principle but less delicate in execution is the method of sealing the known complex in a closed tube, lowering and raising the temperature of a surrounding bath and observing the temperature at which the solid phase appears and disappears; the method can be used at high temperatures at which the materials would disappear by boiling if in open vessels. Thermostatic methods are conducted by stirring or otherwise agitating materials at a fixed temperature until equilibrium has been obtained and then withdrawing a sample of the solution for analysis.

These reliable and well-known methods give data as to the composition of the liquid phase, but give no information at all as to the saturating solid phase. In some instances the solid phase can be removed by filtration and prepared for analysis; but it should be remarked that this procedure requires careful control and, in general, some considerable previous knowledge of the system if error is to be avoided. Such a solid phase is of course always wet with liquid, the complete removal of which is necessary before analysis. The process of removal, and the temperature control of the work must be such that no change in the solid phase occurs; and where the solid is, for example, a hydrate or other compound containing a volatile component, changes in composition are not always easy to avoid. For that reason certain indirect methods of determining the composition of the solid are often more reliable. One such indirect method has already been indicated; where the solid phase is a compound with a congruent melting point, its composition may be taken from the diagram (see Fig. 19) and is the same as that of the coexisting liquid phase.

A second method proposed by Bancroft[1] consists in adding to the system of the two components A and B a small known amount of a third component C which does not enter the solid phase; the ratio of A to C in this complex is written x_1 and that of B to C as y_1. Upon cooling to the temperature at which a solid phase has appeared, the liquid is again analyzed and the ratio of A to C recorded as x_2 and that of B to C as y_2. The change in the ratio of A to C represents the amount of A that has gone into the solid and is therefore $x_1 - x_2$, while $y_1 - y_2$ represents the amount of B which has entered the solid phase; the formula, if it be a compound, is accordingly $(x - x_2)A.(y_1 - y_2)B$. If the solid is a solid solution instead of a compound, its composition is also correctly given, but a second experiment with altered concentrations of *A* and *B* taken must of course give an altered composition of the solid solution.

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[1] Bancroft, *J. Phys. Chem.*, 6, 178 (1902).

By all means the commonest method however of determining the nature of the solid is by a study of the cooling curve for the system, a method proposed by Tammann[1] and almost universally used in the study of alloys, where the mechanical isolation of a solid phase is out of the question. It is clear that if a heated system is allowed to cool with a constant outside temperature environment, the loss of heat will depend upon the heat radiation of the system as a whole, including the container, and the heat changes occurring within the system as a result of alteration in the chemical equilibrium with the temperature. Keeping these two factors in mind, let us plot schematically a cooling curve for a system like that of Fig. 14, starting with a complex *x*; in Fig. 26 we will plot the results, using time and temperature as coördinates. The system is composed of liquid and vapor and is therefore bivariant, so that its temperature may fall without producing any phase reaction; the cooling curve therefore beginning at *a* will be a smooth curve At the temperature at which the solution reaches saturation however, solid phase appears and heat is produced by that phase reaction so that the direction of the cooling curve is altered and the rate of cooling lessened; *b*, the point of discontinuity, is the saturation temperature. The system now consists of three phases and is univariant, permitting the fall of temperature to continue until the eutectic temperature is reached; here occurs, at *c*, a second discontinuity in direction, and what is most important, the temperature will remain constant (the system being now of four phases and invariant) until the liquid has entirely disappeared, the positive heat of formation of the eutectic solids compensating for the loss of heat by radiation. When the liquid has finally disappeared, the system becomes univariant and a cooling curve *de* for the solids follows.

The cooling curve has revealed certain "arrests," *b* and *c*, indicating temperatures pertinent to the study of the system, by repetition under altered circumstances it may also be

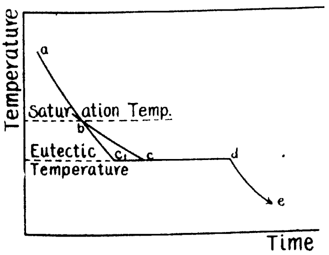

FIG. 26. Cooling Curve for a Two Component System

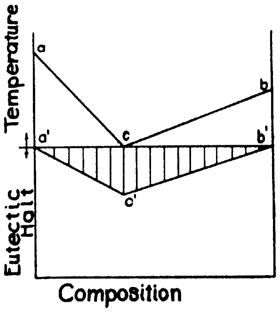

FIG. 27. Eutectic Halt, Showing Composition of Eutectic Solids

made to reveal the desired composition of the solid phase. It is the time of the eutectic halt (i.e., the time interval $c - d$) which may be made to give this information. It is obvious that the duration of the eutectic halt depends upon the quantity of liquid components which change to solid and thus produce the heat which halts the cooling. If amounts of A and B of the same total weight as in the first experiment be taken, but now of the eutectic composition as y in Fig. 14, there will be no "arrest" at any point until the eutectic temperature is reached and the halt will be extended to its maximum, namely, cd, Fig. 26. That composition therefore which gives the maximum eutectic halt establishes the composition of the solid phases at the eutectic. In like manner, a halt will occur at other invariant points, such as a transition point; but if a composition of a compound having a congruent melting point is taken, there will be no eutectic halt, since, as previously pointed out, such a compound acts like an independent component and can therefore have no eutectic. The relationship of the eutectic halt to the composition of these solid phases is rendered clearer by Figs. 27 and 28, in which the duration of the eutectic halt with the composition is plotted directly below the temperature-composition plot; it will be seen that the maximum eutectic halt shows the eutectic composition, and zero eutectic halt shows the composition of pure components and congruently melting compounds. By more extended thermal methods it becomes possible to determine the composition of compounds which do not melt congruently and of solid solutions as well; such methods have been invaluable in the study of metallography.[1]

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[1] *Z. anorg. Chem.*, **37**, 303 (1903); **45**, 24 (1905).

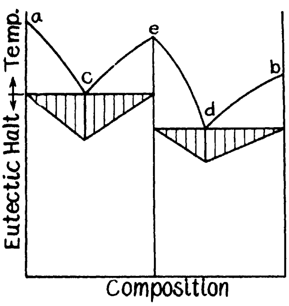

FIG. 28. Eutectic Halt, Showing Composition of Compound and of Eutectic Solids

Another general consideration of interest is the purification of solids by crystallization. Recrystallization of salts from water or of organic compounds from proper solvents is of course a common procedure; it should be noted however that in each of these operations the purpose is to purify from some relatively small quantity of a third component. The separation of a pure substance from a two-component complex is by no means so commonly practiced, nor perhaps so well understood; indeed the separation of two substances by distillation rather than crystallization is employed, not infrequently to the disregard of this simpler method. For purposes of comparison, it may be stated that most substances are volatile, and that therefore a distillation will in the majority of cases yield a vapor consisting of both components, so that tedious fractional distillation is necessary in order to obtain either component reasonably pure; on the other hand, since most substances are mutually insoluble in the solid state, in the majority of instances a pure component can be separated from a two-component solution by the simple process of cooling, and only occasionally is fractional crystallization necessary. With compressed carbon dioxide generally available, temperatures as low as[2] − 78° (its sublimation pressure under one atmosphere pressure) are conveniently obtained, and, in many localities, liquid air is available for production of temperatures down to − 180°, so that the conditions for the separation of many substances by crystallization are not difficult to secure. If the substances used solidify as pure components or compounds, as in the systems illustrated by Figs. 14 to 20, it is necessary only to bring the total composition to a point on the desired side of the eutectic composition, and then to cool the system, stopping however above the eutectic temperature so as not to precipitate the second solid phase. The impurity (i.e., the second phase) is now on, but not in, the second phase; the solid retains the solution possibly by occlusion between crystals, or adsorption upon the surface. Good mechanical separation (the centrifugal machine is invaluable for this purpose) will leave traces only of solution present and a second crystallization of a sample so nearly pure will frequently give material of the highest purity. The usefulness of this method of separating organic compounds, such as various isomers, has not yet been sufficiently realized.

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[1] See Kremann, Die Anwendung der Thermsichen Analyse, Stuttgart, 1909.

[2] Thiel and Caspar, *Z. physik. Chem.*, **86**, 25 (1914).

When, however, the solid phase which forms is a solid solution, it is necessary to resort to a fractional crystallization, just as it is usually necessary to resort to fractional distillation to separate by means of the vapor phase. The nature of the work of a fractional crystallization will be briefly explained.

In Fig. 29 is shown a section of a diagram for a system having solid solutions, it is entirely immaterial what section of a complete diagram it be taken to represent, except in so far as a represents a point of lower temperature, such as the minimum melting point of Curve I, Fig. 23, or the melting point of the pure component in Curve II or III, while b represents a point of higher temperature such as the maximum melting point of Curve III or a melting point of a component. Let a complex x (Fig. 29) be cooled, at c, the freezing point on the liquidus curve, solid begins to appear. Let the complex now be cooled only to the point d, corresponding to the temperature t, at which the system will be only partly solid; the solid phase will now have the composition d'. If these crystals be filtered off, melted and cooled, crystallization begins at the higher temperature t', and the second crop of crystals will have a composition c' between d' and c', depending on the point at which crystallization is arbitrarily stopped. The crystals obtained are therefore approximating the composition b with repeated fractionation, and the liquid is therefore approximating a, how easily or how completely they may be brought to these compositions depends of course on the relative positions of the liquidus and solidus curves for the system, just as a fractional distillation depends on the partial pressures of the components.

If now we compare the section used in Fig 29 with the complete curves of Fig. 23, the following generalization may be made: by a fractional crystallization where solid solution occurs, the solid phase may be brought to the composition of the maximum freezing point, if such exists, or to that of a pure component, while the liquid phase may be brought to the composition of the minimum freezing point, if such exists, or to that of a pure component.

D. THE EQUILIBRIUM GAS-SOLID

Of the three possible diagrams to represent the equilibria between gas and solid phases, namely, the pressure-composition (p-c), pressure-temperature (p-t) and temperature-composition (t-c) diagram, we shall select the first two as most instructive, and as an example will choose a system consisting of a salt and water, where hydrate formation occurs. If we keep the water small enough in amount so that no liquid phase occurs, the possible phases consist of water vapor, anhydrous salt, and as many hydrates as occur. Copper sulphate forms a number of hydrates, namely, $CuSO_4.H_2O$, $CuSO_4.3H_2O$ and $CuSO_4.5H_2O$. Let us examine first the pressure-temperature relations, and insert them in Fig. 30. It must be stated that anhydrous $CuSO_4$ may be kept in contact with water vapor of certain pressures and temperatures without the slightest formation of a hydrate—a fact of primary importance in freeing our minds from the erroneous impression that this compound (or any substance) is a perfect dehydrating agent. The diagram therefore shows an area for the bivariant equilibrium $CuSO_4 + H_2O$, within which both pressure and temperature may be altered simultaneously without altering the number of phases; the formulæ $CuSO_4$ + vapor are printed in this area. If, however, the pressure of water vapor is increased, there comes, for each temperature, a point at which the hydrate $CuSO_4.H_2O$ forms; since three phases are now present, the system is now univariant, and the curve *OC* represents the pressures and temperatures for that equilibrium. The curve is commonly spoken of as the dissociation curve for the monohydrate, since it represents the dissociation pressure of the reaction $CuSO_4.H_2O \rightarrow CuSO_4 + H_2O$ (vapor). If we desire to speak of it as a vapor-pressure curve, it is the vapor-pressure curve for the system $CuSO_4.H_2O - CuSO_4$ – vapor, and not, correctly speaking, for the hydrate alone; for this hydrate has no vapor-pressure curve, but, on the contrary, a vapor-pressure area above the curve. In this area, again, the two-phase system is bivariant, and is bounded above by the vapor-pressure curve for the system $CuSO_4.H_2O - CuSO_4\ 3H_2O$ – vapor. The other areas and vapor-pressure curves may be read from the figure; some of the data are given below.

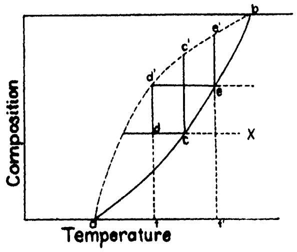

FIG. 29. Fractional Crystallisation

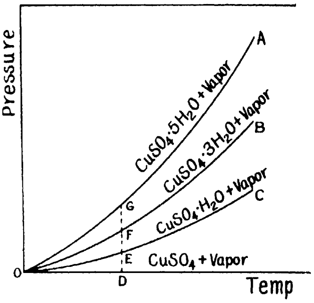
Pressure
A
B
C
$CuSO_4 \cdot 5H_2O$+Vapor
$CuSO_4 \cdot 3H_2O$+Vapor
$CuSO_4 \cdot H_2O$+Vapor
G
F
E
$CuSO_4$+Vapor
O
D
Temp

FIG. 30. Vapor Pressure Curves for Hydrates of Copper Sulfate

A number of conclusions may be drawn from Fig. 30. As to dehydrating efficiency, it is apparent that $CuSO_4$, put in a moist atmosphere or into a non-reacting liquid containing water, will never remove all the water, but will com-

TABLE XXX

DISSOCIATION PRESSURES OF HYDRATES OF COPPER SULFATE[1]

Temp.	$CuSO_4$ $5H_2O$ − $CuSO_4.3H_2O$	$CuSO_4$ $3H_2O$ − $CuSO_4$ H_2O	$CuSO_4$ H_2O − $CuSO_4$
25°	7.8 mm.	5.6 mm.	0.8 mm.
30	11.[illegible]	—	—
35	16.5	11.8	-
40	23.2	-	-
45	32.8	22.1	
50	45.4	30.9	4.5
80	260.1	183.1	

bine with it at a given temperature *D* and reduce the aqueous pressure to a certain definite amount, depending on the quantity of $CuSO_4$ present; if it be so small that it is completely converted into $CuSO_4$ $5H_2O$, the pressure will fall to *G*; if it be larger, so that all the water possible can be taken up without the formation of any hydrate higher than $CuSO_4$ H_2O, the pressure will fall to *E*; but under no circumstances can it fall to zero. The same reasoning applies of course if other salts forming hydrates are used as desiccating agents. Further, it will be seen that, at a given temperature, all three hydrates are perfectly stable and capable of existence; there is no necessary lower limit for the existence of a hydrate in equilibrium with a vapor, although there frequently is a lower limit for its existence in contact with solution. The upper limit of a vapor-pressure curve of this character is reached where there is a congruent melting point or a transition, producing a liquid phase and therefore a new system with a new vapor-pressure curve. That this is the single limitation to the curves at high temperatures is frequently forgotten, and was not at all understood previous to the use of the phase rule; as a result, the student should be on his guard against statements emanating from the older literature to the effect that such and such a hydrate "loses water at 100°," when all that is meant is that the experimenter noticed a rapid loss of water at that temperature, and not that a transition point exists. As Fig. 30 indicates, a given hydrate will lose water at any temperature, if the aqueous pressure is less than that of its dissociation curve; in the terms of the phase rule, since a hydrate and its vapor constitute a bivariant system, they may exist at any pressure, if the temperature is low enough, and at any temperature if the pressure is high enough (provided only that a transition or melting point does not intervene).

A pressure-composition diagram of the same system, given in Fig. 31, shows the conditions at a fixed temperature, taken arbitrarily here as 50° C. If anhydrous copper sulphate be introduced into a vessel and water vapor introduced continuously, the pressure will rise continuously along *ab* from zero pressure to 4.5 mm. before any water is taken up by the salt, since up to *b* the aqueous pressure is less than the dissociation pressure of the mono-

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[1] Chiefly from Carpenter and Jette, *J. Am. Chem. Soc.*, **45**, 578 (1923). See also Wilson, *ibid.*, **43**, 704 (1921); Noyes and Westbrook, *ibid.*, **43**, 726 (1921).

hydrate. At b the monohydrate begins to form, and since there are now two solid phases and vapor present at constant temperature the system is invariant and pressure increase is impossible as long as the three phases coexist. The water vapor continuously introduced is taken up in the formation of the monohydrate, resulting in a change of total composition of the solid phases along the line bc; when the conversion of $CuSO_4$ into $CuSO_4.H_2O$ is complete at c, the pressure again rises without affecting the composition of the monohydrate, along cd, until the dissociation pressure of the trihydrate is reached at d (30 mm.), at which point the trihydrate begins to form. Similar changes in direction of the vapor-pressure curve occur at e, f, and g; the diagram as a whole shows a series of horizontal curves where two solids and vapor are present.

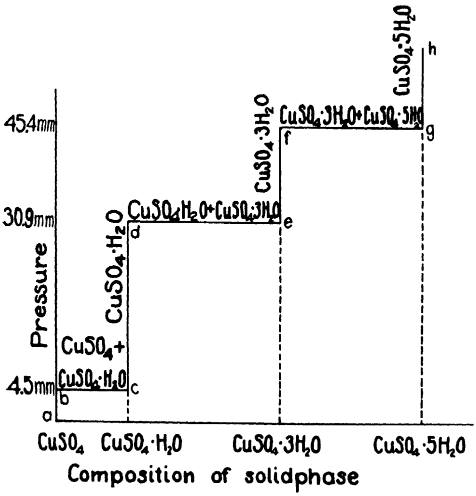

FIG. 31. The System, Copper Sulfate Water. Isotherm at 50° C.

The same general conditions, described above for systems in which a hydrate is formed, are met with in any system in which the two components form a solid compound or compounds, and a vapor composed of one component. Important examples which have been studied include among others the following systems: $CaO - CO_2$;[1] $AgCl - NH_3$,[2] and similar amines; $Hg - O_2$.[3] Systems in which both components are volatile, as in the case of $NH_3 + HCl$ and $NH_3 + CO_2$, exhibit more complicated relations.

The systems discussed or mentioned are characterized by the fact that the solid phases are either pure components or compounds, that is, they are phases of fixed composition. If, however, the vapor phase is taken up by the solid to form a solid solution, a phase of variable composition results and the vapor-pressure curve obtained is quite different from those previously shown. In such a case the pressure-composition diagram is that of Fig. 32, in contrast with that of Fig. 31; as vapor is added, it goes partially into the solid phase to form solid solution, and, since two phases only are present, the curve *ab* results, indicating that the composition of the solid phase is altering with the pressure. If at some pressure *b* a compound forms, there are now three phases present and the system is isothermally invariant, as shown by the curve *bc*. It should also be pointed out that if, at *b*, a *second* solid solution forms, instead of a compound, the curve will take the same direction *bc* since the same number of phases is present. In short, though an ascending curve *ab* of Fig. 32 is proof that a phase of variable composition (solid solution) is being formed and a perpendicular (*ab* of Fig. 31) is proof that there is but one solid phase and of fixed composition present, a horizontal (*bc* of either Fig. 31 or 32) is proof of the existence of two solid phases, and does not distinguish between two compounds and two conjugate solid solutions. Interesting work has been done on systems in which gases form solid solutions, but not always with perfect success; as an example the adsorption of hydrogen by palladium, studied first by Graham and by a host of others, has demonstrated that at least one solid solution is found, but whether there is also compound formation or the formation of a second solid solution is still an open question. Other cases however have yielded more satisfactory results; thus certain "hydrated" silicates and zeolites[1] have been shown to consist of solid solutions of water in the mineral, since they yield a sloping vapor-pressure curve with change of composition (*ab* in Fig. 32), and van Bemmelin[2] has shown, by similar evidence, that various supposed hydroxides, such as $Fe(OH)_3$, $Sn(OH)_4$, $Si(OH)_4$, $Cr(OH)_3$ and probably $Al(OH)_3$, are not compounds but, on the contrary, solid solutions of water in the various oxides. In accordance with this finding, it is proper to speak of these substances as hydrous oxides rather than hydroxides or hydrated oxides, since these latter terms imply definite composition.

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[1] Debray, *Compt. rend.*, **64**, 603 (1867); Le Chatelier, *ibid.*, **102**, 1243 (1883); Riesenfeld, *J. chim. phys.*, **7**, 561 (1909); Zavrieff, *ibid.*, **7**, 31 (1909); Johnston, *J. Am. Chem. Soc.*, **32**, 938 (1910); Jolibois and Bouvier, *Compt. rend.*, **172**, 1182 (1921). Smyth and Adams, *J. Am. Chem. Soc.*, **45**, 1167 (1923).

[2] Isambert, *Compt. rend.*, **66**, 1259 (1888).

[3] Pelabon, *Compt. rend.*, **128**, 825 (1899).

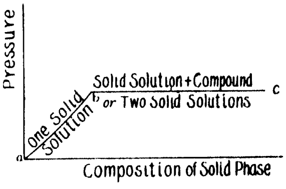

Fig. 32 Isotherm of System Forming Solid Solutions

E. THE EQUILIBRIUM SOLID-SOLID

A type of solid-solid equilibrium which has been referred to only incidentally in the preceding treatment is the equilibrium between two conjugate solid solutions (curves *fe* and *gd* or *gb* in Figs. 24 and 25). It is obvious that such an area of conjugate solutions need not necessarily continue far enough toward higher temperatures to meet the melting-point curves, but may have its consolute point in the solid area just as conjugate liquids may have their consolute point in the liquid area (Fig. 11). The study of such conjugate solid solutions is naturally of great importance in metallography, since phase reactions occurring in the solids must have their effect upon the structure and physical properties of alloys. In general, the establishment of equilibrium between two solid solutions is slow, and is slower at lower temperatures than at higher. The process of annealing solid alloys, i.e., leaving them for long periods at as high temperatures as possible, has the purpose of facilitating the phase reactions, while the process of chilling is resorted to when it is desired to obtain a phase complex which is stable only at high temperatures but which if brought suddenly to low temperatures will remain in metastable equilibrium with changes so slow as to be negligible. The methods by which the phase relations of solid alloys are studied are necessarily much more difficult than those for liquid systems, and may be found described in the texts on metallography; the commonest methods are thermal in character (i.e., use of cooling curves and warming curves) or microscopical. Details as to solid systems cannot be given here, but a brief outline of some of the work on a single such system (the iron-carbon system, important because of the use of such alloys as steel) will be given in order to illustrate equilibria of this class.

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[1] Tammann, *Wied. Ann.*, **63**, 16 (1897), *Z. physik. Chem.*, **27**, 323 (1899).

[2] van Bemmelin, *Ber.*, **11**, 2232 (1878); *ibid.*, **13**, 1466 (1880); *Rec. trav. chim.*, **7**, 37, 87, 106, 114 (1888); *J. prakt. Chim.*, (2) **46**, 497 (1892); *Z. anorg. Chem.*, **13**, 233 (1896).

When iron and carbon (the latter in any reasonably small proportion) are considered, the system is found to give rise to a very considerable number of solid phases, which may enter into various phase equilibria with each other or with the liquid solution of carbon in iron. Leaving the specific properties of these solid phases to be studied elsewhere, if the reader wishes, an enumeration of these solid phases is given below:

$$\text{Three (possibly four) allotropic modifications of iron}\begin{cases}\alpha\text{-ferrite}\\ [\beta\text{-ferrite}]\\ \gamma\text{-ferrite}\\ \delta\text{-ferrite}\end{cases}$$

A carbide of iron, Fe_3C = Cementite

Solid solution of carbon in γ-ferrite = Austenite

Solid solution of carbon in δ-ferrite = ?

$$\text{Two allotropic forms of carbon}\begin{cases}\text{graphite}\\ \text{amorphous carbon}\end{cases}$$

The relationships of these phases have been extensively studied and are embodied in a voluminous literature. There is not an agreement on all of the details, because of the difficulty of the experimental work, but that on which there is common agreement[1] is diagrammed in Fig. 33. Leaving out of consideration the small area near A in which solid solution of carbon in δ-ferrite is found, the principal relationships will be mentioned. γ-ferrite dissolves carbon, giving rise to a solid solution called Austenite, occupying the field $AEHGF$. The dissolving of carbon in the iron brings a fall in the melting point, giving rise to a liquidus curve (AC) and a solidus curve (AE) such as always occurs when solid solution is formed. These curves fall in this case to a eutectic C, as previously shown in Fig. 24; the three phases are a liquid and two conjugate solids, Austenite (*E*) and the carbide of iron Fe_3C known as Cementite (*D*); the eutectic temperature is 1130° C., and the composition is 4.3 per cent carbon. There is of course a second area of conjugate liquid-solid phases, *CBD*, where the solid phase is Cementite. If we now follow the curves of the conjugate solids, *EH* and *DL*, an interruption occurs at the point *H*, where the curve for Austenite (*EH*) meets the curve for the transition of γ-ferrite into α-ferrite (*FGH*). Regarding β-ferrite and α-ferrite as identical except for the occurrence of magnetic properties in the β-ferrite, or adopting any of the other views which have been advanced[1] to the effect that the two

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[1] See Desch, Metallography, 1922, p. 363. Longmans, Green and Co.

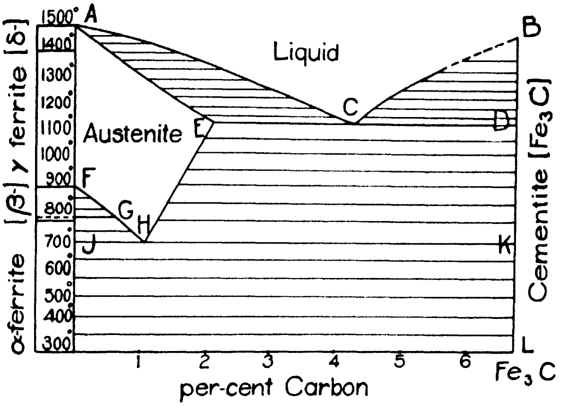

Fig. 33. The System, Iron-Carbon

varieties are not allotropic forms, we may look on the point *F* (900°) as the transition point of pure γ-ferrite into pure α-ferrite, and *FGH* as the curve showing the depression of this transition point by the presence of carbon dissolved in the one solid (Austenite). The intersection of these two curves at *H* (0.89 per cent *C* and 700°) gives a point of equilibrium of three solid phases, namely, α-ferrite, Austenite, and Cementite, and is called a eutectoid; it resembles a eutectic in being the point of equilibrium between two components (here α-ferrite and Cementite) and a solution (here Austenite), differing from the eutectic in that the solution is here a solid solution in place of a liquid solution. At temperatures below the eutectoid there will be two solid phases in equilibrium, namely, α-ferrite and Cementite; these will settle out on cooling in the usual form of a eutectic conglomerate, which, because of its approximation to homogeneity, is looked upon as a structural element and called Pearlite.

By drawing isopleths at the different compositions, it will be easy to see what changes occur when the liquid mass is cooled. Any deductions thus made however are upon the assumption that these various equilibria are attained, and of course metastable conditions may easily persist, particularly if the cooling is rapid. Indeed it has been advanced[2] that all the equilibria here represented are metastable, and that the true equilibrium is one between the two solid phases ferrite and graphite. While the study of the iron-carbon systems from the standpoint of the phase rule is by no means yet complete, it has nevertheless been of very great value in making plain a number of the relationships.

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[1] See Desch, p. 366, for references.

[2] Charpy and Grenet, *Bull. Soc. d'Encouragement*, 1902, 399.

SYSTEMS OF THREE COMPONENTS

In passing to systems of three components, brief study of the new relations of components, variables and degrees of freedom will be helpful. With respect to components, no new principle is involved, but it will be useful to note what general types of reacting substances fall under the heading of ternary systems. Perhaps the most frequently studied cases are those consisting of water with two salts having a common ion, such as $NaCl + KCl + H_2O$; such a system, if it includes new compounds, can have them only of a composition intermediate between that of two or more components, such as double salts or hydrates, and therefore any phase which occurs can have its composition expressed in terms of the three components. It will be noted that a system consisting of water and two salts without a common ion would not fall into the division of ternary systems, since by double decomposition new phases will be produced whose composition is not intermediate between the two salts and water; this very common type of system is a four-component system. On the other hand, two salts without common ion do form a ternary system if water or other substances be absent; although the chemical equation for the double decomposition shows four compounds present, yet any one of them can have its composition expressed in terms of the other three, as was discussed earlier for the reaction

$$CaCO_3 \rightleftarrows CaO + CO_2,$$

where the system was shown to be binary despite the existence of three compounds. A third common instance of a ternary system consists of a single salt and water where the salt suffers hydrolysis, forming basic or acidic salts whose composition again is not intermediate between the salt and water; in this case, the choice of the three components depends upon convenience in representing the system, and an excellent example exists in the case of bismuth nitrate and water, which is most conveniently regarded as having the three components Bi_2O_3, N_2O_5 and H_2O.

The number of independent variables in a ternary system is larger by one than for a binary system, namely, pressure, temperature and two concentration variables, since a ternary solution requires a statement of its composition with respect to two components before its total composition is fixed. The degrees of variance for ternary systems follow directly from substitution in the phase-rule equation; five coexisting phases at a quintuple point give an invariant system, four give a univariant system, three a bivariant and so on.

Graphic Representation of Ternary Systems: Complete representation of all the variables in ternary systems is a complex matter, if at all possible. In most work that has been accomplished such a representation is unnecessary, since the systems studied have been chiefly condensed systems in which the pressure has been kept constant or is ignored. Our problem is therefore to represent the temperature as one variable and the composition as a second. Many geometrical means have been devised for this purpose, of which only one will be discussed and used here, namely, the representation of the composition by triangular coördinates and of the temperature at right angles to the triangular diagram, giving, therefore, a triangular prism as the space figure in which the two variables are represented. At any fixed temperature, the isotherm would then be a triangle, representing the composition, the properties of which will be briefly discussed.

Following the method of Gibbs,[1] an equilateral triangle is chosen and the composition of each pure component represented by a vertex (A, B and C in Fig. 34); the total or unit composition is expressed by the altitude of the triangle, and the fractional part which a particular component contributes to a complex is measured by the perpendicular distance of the point representing that complex from the side opposite the vertex for that component. Thus the point m represents a complex made up of component A in amount proportional to the perpendicular ma, B in the proportion mb, and C in the proportion mc, a representation made possible by the property of an equilateral triangle that the sum of the perpendiculars from a point to the three sides is equal to the altitude of the triangle. For the general properties of the equilateral triangle the reader is referred elsewhere; yet one such property is of such usefulness to our problem as to warrant explicit statement, namely, that if a complex of A and C represented by the point x is taken and increasing amounts of B added, the composition will change along the straight line xB and therefore all points on such a straight line represent the same ratio of A and C to each other.

The discussion of ternary systems must necessarily be abbreviated; a few only of the many possible relationships will be shown under the three following headings.

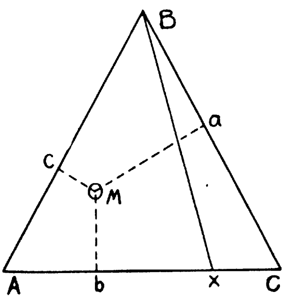

Fig. 34. Equilateral Triangle for Composition of a Ternary System

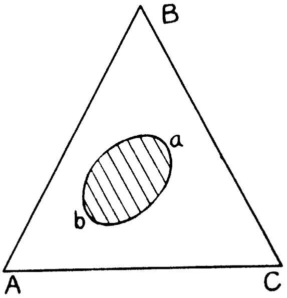

Fig. 35. Ternary System with a Single Binodal Curve

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[1] Gibbs, *Trans. Conn. Acad.*, 3, 176 (1876), Stokes, *Proc. Roy. Soc.*, 49, 174 (1891), Roozeboom, *Z. physik. Chem.*, 15, 984 (1894).

Systems Consisting of Liquid Phases Only: Since any liquids may be solidified or vaporized by suitable temperature changes, it is obvious that we can speak of a ternary system as consisting exclusively of liquids only if the temperature is stated, or in other words, that we are discussing only certain isotherms of a system which will show solid phases at certain lower temperatures. The three liquids taken for study (A, B and C of Fig. 35) are best considered as making up three pairs, $A + B$, $A + C$ and $B + C$; indeed, our ternary systems in general are to be considered as composed of the three binary systems. If each of the three pairs shows unlimited mutual solubility, it usually follows that any ternary mixture also will give a single liquid phase; but this is not universally so, and instances are known in which, within certain limits of concentration, the system separates into two conjugate liquid layers, shown schematically in Fig. 35 by the closed curve *ab*. Within this closed curve tie-lines have been drawn connecting the two conjugate liquids, and any complex taken within that area will separate into two liquid phases represented by the ends of the tie-lines. Such a closed curve has been found for the system water-phenol-acetone[1] at temperatures above 68°, at which all three pairs of components are completely soluble, and has also been found in a few other cases.[2] The boundary curve for this two-liquid area is called a binodal curve, and the interesting character of the points *a* and *b* will shortly be seen.

A single binodal curve is much more often met with where one of the three binary systems shows limited solubility of the liquids. Such a case is that of chloroform, water, and acetic acid (Fig. 36) in which the two components chloroform and water have a limited solubility, giving rise to the two conjugate solutions *a* and *b*. As acetic acid is added to these two liquids it distributes itself between the two phases in unequal amounts and also brings about an increase in the mutual solubility of chloroform and water; any particular tieline, such as *a′b′*, is therefore not parallel to the base of the triangle. Increasing additions of the acetic acid bring the two conjugate liquids nearer and nearer toward each other in composition, until at *k* they become identical; *k* is therefore a critical point, although it is more commonly spoken of as the plaitpoint, and the binodal curve is accordingly a distribution curve of acetic acid in water and chloroform. The figures for the 18° isotherm are given opposite.

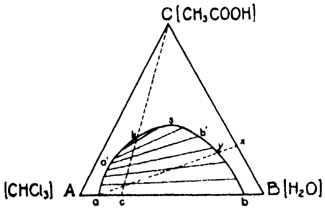

Fig. 36. The System, Chloroform-Water-Acetic Acid, (Schematic)

Distribution curves such as the foregoing have many points of general interest. It will be noted that the distribution ratio of the acid between the two phases is by no means a constant, but varies as the acid brings about changes in the mutual solubility of the chloro-

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[1] Schreinemakers, *Z. physik. Chem.*, **33**, 84 (1900).

[2] Hill, *J. Am. Chem. Soc.*, **44**, 1186 (1922); Hill and Miller, *ibid.*, (1924).

TABLE XXXI

$CHCl_3 - H_2O - CH_3COOH$ AT 18°[1]

Heavy Phase			Light Phase		
$CHCl_3$	H_2O	CH_3COOH	$CHCl_3$	H_2O	CH_3COOH
99.01	0.99	0	0.84	99.16	0
91.85	1.38	6.77	1.21	73.69	25.10
80.00	2.28	17.72	7.30	48.58	44.12
70.13	4.12	25.75	15.11	34.71	50.18
67.15	5.20	27.65	18.33	31.11	50.56
59.99	7.93	32.08	25.20	25.39	49.41
55.81	9.58	34.61	28.85	23.28	47.87

[1] Wright, *Proc. Roy. Soc.*, **49**, 174 (1891), *ibid.*, **50**, 575 (1892).

form and water, as was discussed in the section on the distribution law, a distribution curve which followed the law exactly would be shown by two straight lines running from a to C and from b to C, and in practice no such curves have been found. Again, the plait-point k is almost always found to one side or the other of the maximum point of the curve, S, and therefore is not at the point of the maximum solubility of A and B in each other. If one adds the component C to A and B, the system will pass through the critical point k only if the initial composition is on the line Ckc; any other initial composition will, on addition of C, lead to the disappearance of one phase at the expense of the other rather than in the reaching of the critical state, just as was shown for two-component systems in Fig. 11, where the critical state was reached by change of temperature instead of change of composition at a fixed temperature as in Fig. 36 Other excellent examples of liquid systems showing a single binodal curve are the systems silver-lead-zinc,[2] in which the desilverization of lead is accomplished by the use of molten zinc (Parkes's process), and the system water-toluene-acetone.[3] Such a diagram as Fig. 36, if carefully drawn to scale, gives an accurate method for analysis of a solution of the components B and C, which are otherwise not easily determined if they are organic substances; to the solution of unknown composition, x, the third component A is added from a burette up to the point where the first appearance of a turbidity indicates that the binodal curve (akb) has been reached, the outline of the curve being accurately known, the point where it crosses the line corresponding to the amount of A added (y) is taken, and it follows that the original composition x is on the straight line Ayx.

It is clear from the diagram (Fig. 36) that any complex taken outside of the two-liquid area akb will give a single liquid phase; such a system (liquid + vapor, with temperature fixed) is bivariant, and the composition may be altered with respect to any two of the three components, within the limits of the bivariant area.

Where ternary systems are taken, of which two of the binary systems show limited solubility, two binodal curves are obtained, as in Fig. 37; the diagram offers no points different from those previously discussed. There are, however, some interesting results that follow if the temperature is altered, since the two binodal curves may, generally speaking, be made to expand either by increase or decrease of temperature until they meet. If the juncture at some different temperature occurs at the two plait-points, k and k', the two curves merge into each other to form a continuous band (Fig. 38). Water, phenol and aniline[1] show this condition at temperatures in the neighborhood of 50°. If, on the other hand, the two curves meet in such fashion that the two plait-points do not come in contact, the system shows an area in which three liquid phases are coexistent (*abc* of Fig. 39). This interesting occurrence,[2] found for the systems silver perchlorate-benzene-water and silver perchlorate-toluene-water, may be explained by noting that the solution *a* on the binodal curve which has its base on *AC*, must of course have a solution *b* of the same curve conjugate with it: by like reasoning, since *a* is also on the other binodal curve, there must be a solution *c* conjugate with it on the same binodal curve. The two curves, however, do not of necessity have their tie-lines parallel at the point of their juncture, and therefore *b* and *c* are not the same point; but, since they represent solutions in equilibrium with the same solution *a*, they must be also in equilibrium with each other, giving rise to a tie-line *bc*. There is now a triangular area *abc* representing three liquids and vapor in equilibrium at a fixed temperature; with these five restrictions the system is by rule invariant, or better said, isothermally invariant, and any complex taken within the area *abc* will separate into three coexistent liquid phases of the composition indicated by *a*, *b*, and *c*.

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[2] Bodländer, *Berg- und Huttenmänn. Ztg.*, **56**, 331 (1897).

[3] Walton and Jenkins, *J. Am. Chem. Soc.*, **45**, 2555 (1923).

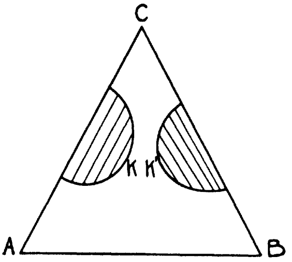

FIG. 37. Ternary System with Two Separate Binodal Curves

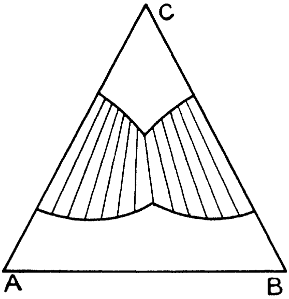

FIG. 38. Ternary System with Two Binodal Curves, Joined at Plait-points

If ternary systems are sought, in which each of the three binary systems shows only partial miscibility, examples will not so readily occur to mind. As a matter of fact, however, some twelve or more cases have been noted and given more or less study; most interesting are the ternary alloy iron-zinc-lead[3] and the system succinic nitrile-water-ether,[4] which latter Schreinemakers has studied exhaustively. In such instances, a three-liquid area such as is shown in Fig. 40 is sure to occur if the three binodal curves can be brought to meet each other by raising or lowering the temperature.

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[1] Schreinemakers, *Z. physik. Chem.*, **29**, 586 (1899).

[2] Hill, *J. Am. Chem. Soc.*, **44**, 1163 (1922).

[3] Timmermanns, *Z. physik. Chem.*, **58**, 159 (1907).

[4] *Z. physik. Chem.*, **25**, 545 (1898).

In the foregoing treatment a series of arbitrarily chosen isothermal sections has been discussed. It will be seen that if a series of such sections for any system be placed in regular order, they would produce a triangular prism, and the binodal curves represented in Figs. 36 to 40 would form the boundary surfaces of loaf-shaped volumes representing the concentration and temperature limits of the conjugate solutions. A line on such a surface joining the plait-points *k* at the different temperatures would be a critical curve, terminating at the point *C* of Fig. 11, on one of the binary surfaces. Such a line might, however, have its point of maximum temperature at a temperature beyond the terminal point *C* of Fig. 11; in that case the maximum point would be in the interior of the prism, and is called a ternary critical point. The development of ternary systems with respect to the temperature axis will be taken up in greater detail in the following section.

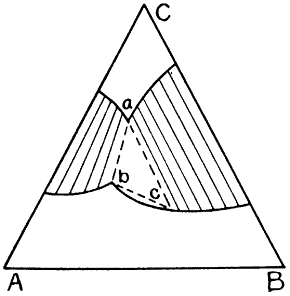

Fig. 39. Ternary System with Two Binodal Curves, Showing Three Liquid Phases

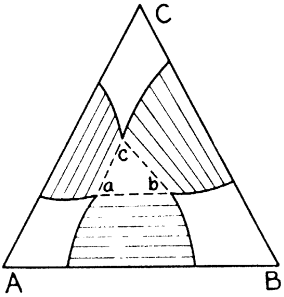

Fig. 40 Ternary System with Three Binodal Curves

Systems Consisting of Solid Phases, With a Single Liquid Phase: In order to visualize the relations that exist in ternary systems when solid phases are present, let us assume that we are dealing with three solid components at some temperature sufficiently below their melting points so that they do not have any effect upon each other; and let us also assume that the solids show no tendency to form solid solutions. If such a mixture of the three solids is subjected to a rising temperature, it will go through a series of changes which have been shown schematically in Fig. 41.

At some temperature a liquid phase will appear, of a composition represented by *a* in sketch I; this will be the temperature at which the three solids, the new liquid phase and the vapor are coexistent, and is therefore a quintuple point and of course invariant; it is spoken of as the ternary eutectic point for the system. If now the temperature rises further, the composition area in which the liquid can exist spreads to some such form as is marked *L* in sketch II. At this higher temperature we can no longer have all three solids in contact with the liquid, since we are above the quintuple point, but a number of different equilibria or phase complexes come into existence, as shown in the diagram. Any complex taken within the area *abc* will give only a liquid and its vapor, and is therefore isothermally bivariant.

Any complex x taken within the triangle Aab will give solid A and a liquid phase of that composition on the line *ab* at which the tie-line from *Ax* passes through *ab*; the system, consisting of solid, liquid and vapor, is isothermally univariant, and if any change in the amount of either *B* or *C* is made, the composition of the liquid phase which forms is at once fixed, as shown by the tie-lines. The same discussion applies to the two other triangles

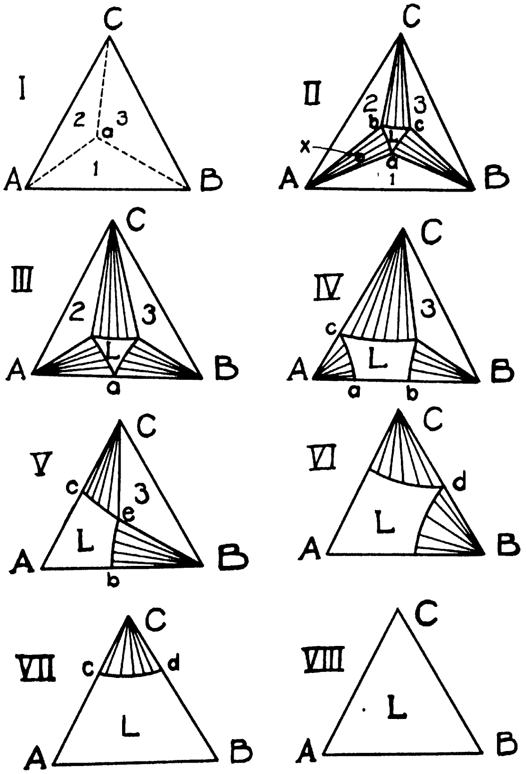

FIG. 41. Ternary Systems, with a Single Liquid Area

Bac and *Ccb*. Finally there are present three triangular areas marked 1, 2 and 3; these represent isothermally invariant areas, within which any total complex will change into two solids and a liquid, as represented by the vertices of the triangles, together of course with vapor.

As the temperature is raised further, the system goes through a variety of changes (III to VIII) which reduce the number of equilibria one by one. In III the point *a* has moved until it touches the base-line *AB*; this is a temperature at which a binary liquid composed of *A* and *B* is in equilibrium with the two solid components, and will be recognized at once as the eutectic for the binary system *AB* (point *C*, Fig. 14). In sketch IV, the liquid has reached the binary eutectic for *A* and *C* at the point *c*. This extension of the liquid area *L* has, it will be seen, terminated successively the invariant equilibria 1 and 2. At higher temperatures the liquid area has spread along *AB* (sketch IV) and this movement is describing the two solubility curves on the binary surface *AB* (lines *CR* and *CM* of Fig. 14). In sketch V the point *a* has reached the freezing point of *A*, and the equilibrium of solid *A*, liquid and vapor shown as *Aac* in sketch IV has disappeared. Sketch VI shows the liquid area reaching the binary eutectic for *B* and *C* at *d*, terminating the invariant equilibrium 3, and sketch VII shows that the freezing point of *B* has been reached. With increasing temperature the solubility curve *cd* rises until, when the freezing point of *C* has been reached in sketch VIII, the system will give a liquid phase whatever composition is taken. It will be seen that the fixed temperatures in such a system consist of a single quintuple point (the ternary eutectic), of three binary eutectics and three freezing points of components.

Some of our best known ternary systems have isotherms like those shown in Fig. 41. Thus, for example, Schreinemakers[1] found that the 30° isotherm for the system $(NH_4)_2SO_4$-NH_4Cl-H_2O is exactly like sketch V, where *A* stands for H_2O, *B* for NH_4Cl and *C* for $(NH_4)_2SO_4$; the solution *e*, saturated with respect to both salts, contains 17.6 per cent of NH_4Cl and 25.7 per cent of $(NH_4)_2SO_4$, while *b*, saturated with NH_4Cl alone, contains 29.5 per cent of that salt and *c* contains 44 per cent of $(NH_4)_2SO_4$. Such a diagram (V) will in general express the relations of two salts in water at laboratory temperature, which is above the melting point of ice, above the eutectics for water with each of the salts, and, of course, below the eutectic for the two salts alone.

A simple extension of the diagrams of Fig. 41 will suffice for cases where two components form a compound, called a binary compound, or where all three unite to form a ternary compound. The composition of any binary compound will be expressed by a point on one of the sides of the triangle, while that of a ternary compound will fall within the triangle.

The interesting system of bismuth nitrate and water will afford an example showing ternary compounds; as previously explained, this is a three-component system, and is diagrammed with Bi_2O_3, N_2O_5 and water as the three components. Fig. 42 shows schematically the relationships as found by Rutten and van Bemmelen[2] for 20°. The system at this temperature shows four ternary compounds which are marked I, II, III and IV in the figure. The composition of each is given below.

Point in Fig 42	Composition	Conventional Formula
I	$Bi_2O_3\ N_2O_5\ 2H_2O$	$BiONO_3\ H_2O$ (basic salt hydrate)
II	$Bi_2O_3\ N_2O_5\ H_2O$	$Bi_2O(NO_3)_2(OH)_2$ (basic salt hydrate)
III	$Bi_2O_3\ 3N_2O_5\ 10H_2O$	$Bi(NO_3)_3\ 5H_2O$ (normal salt hydrate)
IV	$Bi_2O_3\ 3N_2O_5\ 3H_2O$	$Bi(NO_3)_3\ 1\frac{1}{2}H_2O$ (normal salt hydrate)

It will be seen that each of these solid phases may be in equilibrium with solutions varying in composition over a limited range (*ab*, *bc*, *cd*, *de*) and that two solid phases can be in equilibrium only with a solution of fixed composition, as shown by the triangles having *b*, *c*, and *d* as their angles.

With these several types of isotherms before us, it will not be difficult to construct a picture of the triangular prism that will show the temperature as a variable, and of which the isotherms studied are simply cross-sections. Fig 43 shows such a diagram. The point *d* is the ternary eutectic, or quintuple point, below which all mixtures of the components can exist only in the solid state. The points *a*, *b* and *c* are the three binary eutectics for the three two-component systems, and *e*, *f* and g are the melting points of the three components. The three shaded surfaces separate the region of solid phases below from the region of liquid phases above. These surfaces represent a single solid phase (*B* for *bgad*, etc.) in equilibrium with liquid, the lines *ad*, *bd* and *cd* represent two solid phases in equilibrium with liquid, and the point *d* represents the three solids with liquid. If then we consider any liquid of composition above the diagram as cooled down gradually, it will precipitate a single solid phase where the isopleth passes into one of the surfaces, and as the temperature continues to drop, the composition of the remaining liquid must begin to vary along this surface as more and more of the one component settle out, until a point is reached on one of the eutectic curves *ad*, *bd* or *cd*. Here a second solid will begin to precipitate and the composition and temperature of the solution will vary along the specific eutectic curve until finally, at *d*, the system becomes invariant (three solids, liquid and vapor) and no change in composition of the liquid occurs while it is solidifying completely. It is clear that a knowledge of such a complete diagram for a ternary alloy will enable the metallurgist to foretell in what order and fashion the three components will solidify from a given complex taken. Further, since the ternary eutectic is necessarily lower than all the binary eutectics, it becomes possible to contrive especial low melting alloys of three components; the following examples will illustrate the point.

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[1] *Z. physik. Chem.*, **69**, 557 (1909).

[2] *Z. anorg. Chem.*, **30**, 342 (1902).

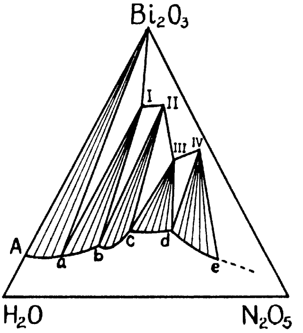

FIG. 42. The System Bi_2O_3 — N_2O_5 — H_2O (Schematic)

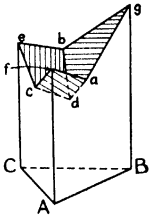

FIG. 43 Ternary System Showing Ternary Eutectic

TABLE XXXII

EUTECTICS IN TERNARY ALLOYS

Pb — Bi — Sn [1]			Pb — Bi — Cd [2]		
M.P. of Component	Binary Eutectic	Ternary Eutectic	M.P. of Component	Binary Eutectic	Ternary Eutectic
Pb = 325°	Pb + Bi = 127°	96°	Pb = 320°	Pb + Cd = 245°	92°
Bi = 268°	Bi + Sn = 133°		Cd = 320°	Cd + Bi = 145°	
Sn = 232°	Pb + Sn = 182°		Bi = 270°	Pb + Bi = 125°	

[1] Charpy, *Compt. rend.*, **126**, 1569 (1898).

[2] Bartow, *J. Am. Chem. Soc.*, **32**, 1410 (1910).

Systems With Several Solid Phases and Several Liquid Phases: It is possible now, with the information gained in the previous two sections, to discuss any isotherm of any condensed system without bringing in any relationships not already met with. Any isotherm will show only the following parts, which can all be found in Figures 35 to 42: binodal curves, solubility curves, and isothermally invariant triangles, which later may connect at their vertices three solids (Fig. 41, I, *ABC*), two solids and one liquid (Fig. 42, I, II, *b*), two liquids and one solid (shown later in Fig. 44, *Acd*), or three liquids (Fig. 40, *abc*). Of course, the number of such equilibria at a given temperature may be either small or large, and the possibilities of combinations are very many indeed and only a relatively small proportion of them have thus far been investigated. Two such cases will be shown here.

Fig. 44 shows a fairly common type of ternary isotherm occurring when two mutually soluble liquids *C* and *B* are treated with a single solid which is freely soluble in one of them and sparingly soluble in the second. Such a case will be more readily recognized if the usual laboratory method of preparing it is stated. If we have a saturated aqueous solution of some inorganic salt, such as potassium fluoride in water, and add alcohol to it, the alcohol at first passes into the liquid phase, but on continued addition finally gives rise to a second liquid phase; the mutual solubility of the two liquids in each other has been diminished by the presence of the salt. The triangle *Abd* represents the solid salt in equilibrium with solution consisting of water with more or less alcohol, along the solubility curve *bd*, the triangle *Aac* in like fashion represents the salt in equilibrium with solutions chiefly alcoholic in content, and since the solubility of the salt in alcohol is usually small, the point *a* is close to *B* and the curve *ac* is short The triangle *Acd* shows an isothermally invariant equilibrium of the two saturated solutions *c* and *d* in contact with solid salt *A* The curve *ced* is a binodal curve for the two liquid phases that are in equilibrium with each other, as shown by the tie-lines, and, finally, the area *BCbdeca* is the area for the bivariant solution, and shows the limits within which the three components will form a single liquid solution. Such systems as the above occur in the organic laboratory in the familiar operation of "salting out" one liquid from another by addition of a properly chosen salt. by addition of it to saturation, the complex will fall in the triangle *Acd*, and, since the solutions *c* and *d* cannot vary in composition at a fixed temperature, it is obvious that further addition of salt after solid phase appears is of no effect. In addition to numerous cases of the above type in which the isotherm

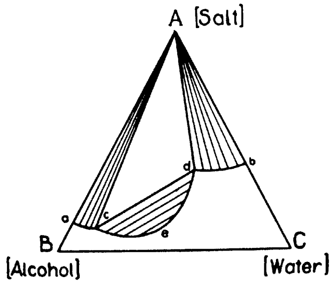

FIG. 44. The System, Alcohol-Water-Salt

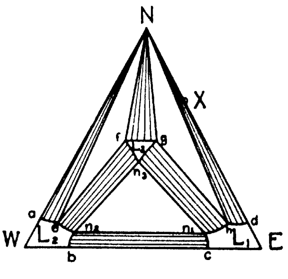

FIG. 45. The System Succinic Nitrile-Ether-Water (Schematic)

is known qualitatively, a considerable number have been studied quantitatively; the work of Frankforter[1] and others gives excellent examples.

Fig. 45 represents no such familiar type of isotherm as the preceding, but is selected to show that a large number of equilibria frequently come into being in ternary systems. Schreinemakers[2] found for the system water-ether-succinic nitrile that twelve different equilibria or phase complexes exist at 2°, as shown in the figure and enumerated below:

3 areas for 1 liquid phase (marked L_1, L_2, L_3) = bivariant,
3 areas for 2 liquid phases (efn_3n_2, ghn_1n_3, cbn_2n_1) = univariant,
3 areas for 1 solid + 1 liquid (Nae, Nfg, Nhd) = univariant,
2 areas for 1 solid + 2 liquids (Nfe, Ngh) = invariant,
1 area for 3 liquids ($n_1n_2n_3$) = invariant.

It will appear that in such a system as this, if one took an amount of nitrile and ether represented by the point X and added water to it at this temperature, the changes will be those shown on a line running from X to W; there will be seven entirely different complexes obtained by the formation and disappearance of phases, which the student can tabulate by comparing the list of phases present in the first area *Nhd* with those found in each area crossed successively by the line.

Space does not permit a discussion of the complete diagrams that have been worked out to show the effect of changing temperature upon complex ternary systems such as the foregoing. It will be apparent, however, that where the coexistence of three liquid phases is possible and where there are three solids possible (or more if binary or ternary compounds exist) as well as a vapor, a considerable number of quintuple points may be looked for at which five phases are coexistent. The ternary eutectic shown in Fig. 43 is by no means the only point of fixed temperature found in ternary systems; wherever five phases are found to coexist, the temperature will remain perfectly stationary upon addition or subtraction of heat until one of the phases disappears. Where complete studies of ternary systems like that of Fig. 45 have been made, a considerable number of these fixed points have been met with; thus, the system silver perchlorate-water-benzene[3] shows six quintuple points, ranging from − 58.4° to + 42.1°, and eighteen monovariant equilibria.

Many interesting examples of condensed ternary systems have been studied in detail, the system potassium chloride-magnesium chloride-water was investigated by van't Hoff and Meyerhoffer[4] as part of an extremely valuable research on the Stassfurt salt deposits; the system ferric chloride-hydrogen chloride-water[5] is of interest in showing the effect of the acid upon the concentrations in which the various hydrates of ferric chloride can exist. In addition to studies of condensed systems such as the foregoing, there has been much valuable work on ternary systems in which liquid phases are absent; the study of the system iron-carbon monoxide-carbon dioxide[6] has given much useful information relative to the types of reaction occurring in the blast furnace and in hydrogen manufacture.

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[1] Frankforter and Frary, *J. Phys. Chem.*, **17**, 402 (1913). Frankforter and Bell, *J. Am. Chem. Soc.*, **36**, 1103 (1914).

[2] *Z. physik. Chem.*, **25**, 543 (1898).

[3] Hill, *J. Am. Chem. Soc.*, **44**, 1169 (1922).

[4] *Z. physik. Chem.*, **27**, 75 (1898); **30**, 86 (1899).

[5] Roozeboom and Schreinemakers, *Z. physik. Chem.*, **15**, 588 (1894).

[6] Baur and Glaessner, *Z. physik. Chem.*, **43**, 354 (1903). Chaudron, *Ann. Chim.*, **16**, 221 (1921). Eastman and Evans, *J. Am. Chem. Soc.*, **46**, 888 (1924).

Indirect Analysis of Solid Phases: In the discussion of binary systems, it was pointed out that direct analysis of solid phases is beset with difficulties, and that it is usually necessary to resort to indirect analysis, thermal methods being the simplest. In condensed ternary systems thermal analysis is also possible, but it happens that other methods are available which are much simpler in execution—indeed, much simpler than for binary systems. Bancroft[1] has given the simplest exposition of this method, although it has also been proposed by Schreinemakers and others. In Fig. 46 let *ab* be a portion of a solubility curve, and the problem be to determine whether the solid phase is pure *B*, some compound of *A* and *B*, or a ternary compound of *A*, *B* and *C*.

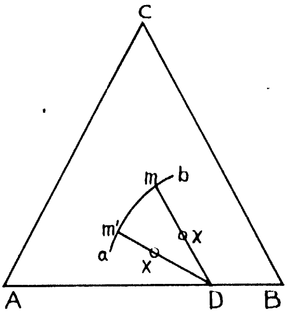

Fig. 46 Indirect Analysis for Solid Phase in a Ternary System

Let a complex x be made up by weight, brought to equilibrium with its saturated solution and the composition of the solution found by analysis to be m, then, as pointed out for other isothermally univariant equilibria, the tie-line mx and its prolongation must connect the compositions of the liquid phase and the solid phase, and the solid must therefore lie somewhere along mx. Let the experiment be repeated with a second complex x' giving a solution m'; by the same reasoning the solid falls upon the prolongation of the tie-line $m'x'$. The only composition fulfilling both these requirements is that shown by the intersection of the two lines, here shown as D, and indicating that the solid phase is a binary compound of A and B and of the composition D. If the solid phase were the pure component B, the two tie-lines would intersect at B; if it were a ternary compound, they would intersect within the triangle, and if it were a solid solution of A and B, they would intersect at some point outside the triangle. The trial with a third tie line would distinguish between a ternary compound, where all lines would intersect at a point within the triangle, and on the other hand a ternary solid solution, shown by the failure of the lines to intersect at a single point, the three intersections, however, would fall within the triangle The method is as simple in its experimental execution as it is straightforward in its logic.

SYSTEMS OF FOUR AND FIVE COMPONENTS

For consideration of systems of more than three components, the reader is referred to the text-books on the phase rule. Work on systems of four or more components is necessarily more difficult than on simpler systems, and the graphical representation of results is necessarily more complicated; nevertheless, a considerable amount of valuable work has been done on such systems, including the study of a number of reciprocal salt pairs in water,[2] which is the convenient term for metathesis or double decomposition occurring in aqueous solution, and including such important technical reactions as the manufacture of potassium nitrate from sodium nitrate[1] and the ammonia process for manufacturing sodium bicarbonate.[2]

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[1] *J. Phys. Chem.*, **6**, 178 (1902).

[2] Meyerhoffer and Saunders, *Z. physik. Chem.*, **28**, 453 (1899); **31**, 370 (1899).

THE SOLUBILITY OF SOLIDS IN LIQUIDS

In the preceding sections it has been shown that there exist two fundamental laws according to which the behavior of heterogeneous systems can be classified —namely, the distribution law and the phase rule. While each of these laws has proved of great use, it will be noted that neither of them gives an answer to the most natural question which a heterogeneous system suggests, that is, what determines the extent to which one phase dissolves in another? This question has received no completely satisfactory answer from any source, but it is nevertheless true that by means of a number of laws of more limited scope than the distribution law and the phase rule, and by means of a number of theories, it is possible to predict in many cases what the solubility of the one phase in the second will be and to calculate such solubilities with considerable accuracy. In this section attention will be given to such methods of study as have given these partial answers; and because of the marked difference in the behavior of non-electrolytes and electrolytes, the two classes will be treated separately.

Solubility of Non-Electrolytes: It has been known for a very long time that substances which are closely related chemically will show marked solvent action upon each other, while those which are dissimilar in constitution and chemical properties will ordinarily display much less solubility. The time-honored rule, *similia similibus solvuntur*, is an expression of this observation. When the advances in organic chemistry made it possible to determine the constitution of compounds, like and unlike came to have a more definite meaning, and the rule capable of a more definite application. A list of the commoner classes of organic compounds on the basis of their chemical relationship follows;[3] any compounds occurring in classes adjacent to each other will, according to the rule, show high mutual solubility, while a wide displacement of two compounds in the table generally indicates low solubility.

TABLE XXXIII

Classification of Compounds on Basis of Chemical Relationships

(1) Water
(2) Fatty acids
(3) Alcohols
(4) Ketones
(5) Aldehydes
(6) Nitriles
(7) Phenols
(8) Aromatic aldehydes
(9) Ethers
(10) Halogen-substituted hydrocarbons
(11) Carbon disulfide
(12) Aromatic hydrocarbons
(13) Aliphatic hydrocarbons

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[1] Uyeda, *Mem. Coll. Sci.*, Kyoto II, 245; Reinders, *Proc. K. Akad. Wetenschap. Amster.*, **16**, 1065 (1914).

[2] Fedotieff, *Z. physik. Chem.*, **49**, 162 (1904).

[3] Rothmund, *Z. physik. Chem.*, **26**, 489 (1898).

In the qualitative application of this rule, it is necessary of course to bear in mind that the chemical character of a compound is determined not by a single group but by the whole constitution of its molecule, so that, for example, a fatty acid of high carbon content, like palmitic acid, is to be viewed as a hydrocarbon rather than an acid, and therefore is quite insoluble in water but freely soluble in those classes of compounds found further down in the list.

A much more successful approach to the question has been made by way of the freezing-point laws. It has previously been shown in our discussion of phase-rule diagrams that a freezing-point curve is nothing more nor less than a solubility curve, since it indicates the composition of the liquid phase in equilibrium with the solid phase at a given temperature and pressure. The law of Raoult, according to which the freezing point of any substance is depressed equally by equimolecular quantities of all substances, would give us a mathematical expression for the solubility curve of any two substances if it were a law of universal applicability; but, as is well known, it is commonly applied only over a small concentration range (which would mean for only a few degrees below the melting point of the pure solute), and is subject to limitations in many instances in which it is necessary to assume polymerization. Starting with the law of Raoult and studying the deviations of various substances from that rule, Hildebrand[1] and his co-workers and Mortimer[2] have evolved a treatment by which solubility may be calculated in many instances with a fair approximation to accuracy. If Raoult's law holds for a given case, the solubility N of a given solid, expressed as a molar fraction, will be proportional to $\frac{P'}{P}$, where P' is the partial pressure of the solute and P the vapor pressure which the pure solute would show in liquid form at that temperature (a value obtained by extrapolation); since these two pressures are related by Raoult's law, we may write

$$\frac{P'}{P} = \frac{n_1}{n_1 + n_2} = N.$$

Now, the relationship of the partial pressure P' to the pressure of the pure solute P is expressed in the Clausius-Clapeyron equation

$$\log \frac{P'}{P} = \frac{-L_0}{4.58T} + \frac{\Delta C}{1.99} \log T + I,$$

in which L_0 is the molal heat of fusion of the solid at the absolute zero, ΔC is the difference in the specific heats per mol. of the liquid and solid form, and I is an integration constant whose value is obtained by putting for T the melting point on the absolute scale, at which $\log \frac{P'}{P} = 0$.

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[1] Hildebrand et al., *J. Am. Chem. Soc.*, **38**, 1452 (1916); **39**, 2297 (1917); **41**, 1067 (1919); **42**, 2180 (1920); **43**, 500, 2172 (1921); **45**, 682 (1923); *Phys. Rev.*, **20**, 52 (1923).

[2] *J. Am. Chem. Soc.*, **44**, 1416 (1922); **45**, 633 (1923).

Following the above argument, when a substance follows Raoult's law in a given solvent, its solubility can be calculated by the above formula; the curve for this equation, representing the change of solubility with the temperature, would be an ideal solubility curve. In practice however many substances diverge from this ideal curve very widely; Hildebrand ascribes these anomalies chiefly to inequalities in the internal pressure and to the polarity of the substances, and deduces that non-polar substances having approximately equal internal pressure will obey Raoult's law and may have their solubility calculated by the above formula, whereas inequalities in internal pressure lead to positive deviations from the law. A list of various compounds, arranged in order of their internal pressures as calculated by various methods, is very similar to the list given in Table XXXIII based simply upon chemical relationships. Mortimer has shown how, in a table of compounds thus arranged, a factor may be derived for any two compounds which, if introduced into the thermodynamical equation previously given, compensates for these deviations from Raoult's law and gives an approximately correct figure for the solubility.

Solubility of Electrolytes in Water: The attempt to find a basis for calculating the solubility of electrolytes in water has met with only a small degree of success. Abegg and Bodländer[1] have evolved a theory according to which the solubility of a salt in water depends upon the electro-affinity of its ions, defining the electro-affinity as the energy change necessary to change an atom to an ion, not measured against a normal solution, as in the measurements of electromotive potential, but between an equal concentration of ions and atoms. The theory has had but limited applicability, giving a substantially correct order of solubility for such relatively insoluble salts as the silver halides and similar salts of thallium.

On the other hand, an extended and valuable theory has been evolved by which, taking the solubility of a salt in water as given, the effect of a second salt in increasing or diminishing the solubility of the first can be calculated. As will be shown, this theory is adequate to give a qualitative measure of the solubility changes in all cases, and has been adopted almost universally in explaining and predicting the results obtained in analytical practice; examined quantitatively, it will be shown to be in general harmony with the experimental results, though in no case does it give agreement within the limits of experimental error. The theory will therefore be presented with the understanding that it consists of a series of principles which are only approximately correct, and a discussion of their inherent error will follow.

It has long been known that the presence of an excess of a precipitant (i.e., a salt having an ion in common with the precipitated compound) causes a depression in solubility, while the presence of any other salt brings about an increase in solubility. It was not however until the theory of electrolytic dissociation had been advanced by Arrhenius[2] that it became possible to explain these well-known facts by means of an acceptable theory. Nernst[3] was the first to advance the principles upon which such an explanation can be built up, and they were clearly stated by A. A. Noyes[4] as follows:

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[1] Bodländer, *Z. physik. Chem.*, 27, 55 (1898); Abegg and Bodländer, *Z. anorg. Chem.*, 20, 453 (1899).

[2] *Z. physik. Chem.*, 1, 631 (1887).

[3] *Z. physik. Chem.*, 4, 372 (1889).

[4] A. A. Noyes, *Z. physik. Chem.*, 6, 241 (1890).

1. "In a saturated solution of a partially dissociated substance, the concentration of the undissociated part remains constant, even if another dissociated body is added." This is the principle of the constant solubility of undissociated molecules or of the constant molecular solubility, and is founded upon a plausible analogy to the behavior of a non-electrolyte; if a solution is saturated for example with sugar, the addition to the solution of some other compound such as salt should be without effect upon the solubility of the sugar, provided of course that there is not chemical interaction between the sugar and the salt and that the solutions are dilute; the principle is therefore similar to Dalton's law of partial pressures for gases, as applied to dilute systems where there is no chemical interaction.

2. The product of the active masses of the ions of the substance with which the solution is saturated has a constant value. This is the principle of the constancy of the ion product, or, as it is more commonly known, the principle of the constancy of the solubility product. It can be shown that the two foregoing principles are not independent, but that either one can be derived from the other by means of the concentration law. If a salt AB is undergoing reversible dissociation, the equilibrium is expressed as follows:

$$AB \rightleftarrows \overset{+}{A} + \overset{-}{B}.$$

Applying the concentration law to this equilibrium at saturation, we have

$$\frac{C_{\overset{+}{A}} \times C_{\overset{-}{B}}}{C_{AB}} = K.$$

Now, if the first principle given above be accepted, the concentration of the undissociated molecules, C_{AB}, has a constant value, whence

$$\frac{C_{\overset{+}{A}} \times C_{\overset{-}{B}}}{K'} = K$$

and

$$C_{\overset{+}{A}} \times C_{\overset{-}{B}} = KK' = K''.$$

3. A third principle implied and used in the experimental work of Nernst, Noyes and all others who have contributed to the theory is that some form of dilution formula can be written to express the dissociation equilibrium of each of the electrolytes present in the solution. Such a dilution formula must necessarily express not merely the dissociation of the compound, but whatever effect (if any occurs) there may be exerted upon it by the presence of other ions and other molecules which do not enter into direct chemical action with the electrolyte in question. In the course of twenty-five years of experimental work on these solubility problems most of the dilution laws discussed in the chapter on electrolytic dissociation have been used at one time or another, the simple Ostwald dilution law[1] has been used (correctly applied of course only to weak electrolytes), van't Hoff's[2] formula has been used, and the later work has been done with the use of Bancroft's[3] formula modified by the isohydric principle of Arrhenius,[4] so as to take into account the effect of the molecules and ions of the other compounds present. Some form of dilution formula is essential to every calculation, and it will at once be seen that all of the questions involving the accuracy of our methods of determining the degree of dissociation of an electrolyte must also affect the theory by which we calculate changes in solubility.

The test of the accuracy of these three solubility principles lies obviously in determining whether we can correctly calculate the solubility of a given salt in the presence of known quantities of a second salt. The work of Nernst and of Noyes gives examples of this type of calculation. The mathematical difficulties are least where the second salt has an ion in common with the saturating salt, since the number of molecular species present in the solution is then a minimum. Treating the case algebraically, let a solution be saturated with a salt AB and let a given amount (n) of a soluble salt CB be added; the equilibrium is

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[1] Ostwald, *Z. physik. Chem.*, 3, 170 (1889).
[2] van't Hoff, *Z. physik. Chem.*, 18, 300 (1895).
[3] Bancroft, *Z. physik. Chem.*, 31, 188 (1899).
[4] Arrhenius, *Z. physik. Chem.*, 2, 284 (1888), 31, 197 (1899).

$$AB + CB \rightleftharpoons \overset{+}{A} + 2\overset{-}{B} + \overset{+}{C}.$$

The terms known and unknown may be tabulated as follows:

Known

Total solubility of AB in pure water $= m_0$
Total conc. of CB added $= n$
Dilution constant for CB $= k_b$
Molecular solubility of AB $= k_a$
Solubility product of AB $= k$

Unknown

Conc. of molecular AB $= a$
Conc. of molecular CB $= b$
Conc. of A ions $= A$
Conc. of B ions $= B$
Conc. of C ions $= C$
Total solubility of AB $= m$

To solve for m, the total solubility of the salt, six equations can be written; the first three are based on the fundamental assumption of the dissociation theory, that the total concentration of any electrolyte is that of its undissociated molecules plus that of its ions, the fourth is a dilution formula for the salt CB, the fifth expresses the principle of the constancy of molecular solubility and the sixth that of the constant solubility product. The equations follow:

$$\begin{aligned} &(1)\quad m &&= A + a,\\ &(2)\quad m + n &&= a + b + B,\\ &(3)\quad n &&= C + b,\\ &(4)\quad \frac{C \times B}{b} &&= k_b,\\ &(5)\quad a &&= k_a,\\ &(6)\quad A \times B &&= k. \end{aligned}$$

The number of equations is sufficient for algebraical solution for m, but it has been usual to adopt the shorter methods of approximation. In the following table, showing results obtained by Noyes,[1] the values of k_a, k and k_b were taken from independent measurements of the electrical conductivity of the salts in question, and equation (4) was modified from the form given above (Ostwald's dilution formula) to take into account the total concentrations of all ions present (Arrhenius's isohydric principle). The results follow.

TABLE XXXIV

SOLUBILITY OF SALTS IN PRESENCE OF SALTS WITH A COMMON ION
$AgBrO_3$ with $AgNO_3$ and with $KBrO_3$ (24.5°)

Added Salt (n) (normality)	Solubility on Addition of $AgNO_3$	Solubility on Addition of $KBrO_3$	Calculated Solubility
0.........	.00810	.00810	—
0.00850....	.00510	.00519	.00504
0.0346.....	.00216	.00227	.00206

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[1] *Loc. cit.*

TlCl with $TlNO_3$ and with HCl

Addition	Solubility on Addition of $TlNO_3$	Solubility on Addition of HCl	Solubility Calculated
0	.0161	.0161	—
0.0283	.00830	.00836	.00783
0.0560	.00571	.00565	.00508
0.1468	.00332	.00316	.00253
1.0000	—	.00200	—

There is reasonable agreement between the observed and the calculated results, although the deviation amounts in most cases to several per cent. A much closer agreement between theory and practice is found when the saturating salt has a very small solubility, in such cases it is also possible to make additional assumptions which simplify very greatly the process of calculation. Examples are found in cases of double decomposition in which two insoluble salts are concerned, of which the following have been studied

$TlCl + KCNS \rightleftarrows TlCNS + KCl$ (Knuppfer[1]),
$PbI_2 + Na_2SO_4 \rightleftarrows PbSO_4 + 2NaI$ (Findlay[2]),
$CaCO_3 + K_2C_2O_4 \rightleftarrows CaC_2O_4 + K_2CO_3$ (Foote[3]),
$2AgCl + 2KOH \rightleftarrows Ag_2O + 2KCl + H_2O$ (Noyes and Kohr[4]),
$BaC_2O_4 + CaCl_2 \rightleftarrows CaC_2O_4 + BaCl_2$ (Foote and Menge[5]),
$BaCO_3 + CaCl_2 \rightleftarrows CaCO_3 + BaCl_2$ (Foote and Menge),
$BaF_2 + CaCl_2 \rightleftarrows CaF_2 + BaCl_2$ (Foote and Menge),
$AgCl + KCNS \rightleftarrows AgCNS + KCl$ (Hill[6]),
$AgCNS + KBr \rightleftarrows AgBr + KCNS$ (Hill),
$AgBr + KI \rightleftarrows AgI + KBr$ (Hill).

In each of these cases two quite insoluble salts appear. Representing them by the symbols AB and CB (for they have one ion in common in each case), the principle of the constant solubility product would give the following equations:

$$C_A \times C_B = K_1,$$
$$C_C \times C_B = K_2.$$

Now if the salts are very insoluble, their concentration must be very low, and we may therefore assume practically complete dissociation. On this assumption, it follows that the solubility of each of the salts (S_1 and S_2), expressed in equivalents, is equal to the concentration of either of its ions, whence it follows that

$$C_A \times C_B = S_1^2,$$
$$C_C \times C_B = S_2^2.$$

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[1] *Z. physik. Chem.*, **26**, 255 (1898).
[2] *Ibid.*, **34**, 407 (1900).
[3] *Ibid.*, **33**, 740 (1900).
[4] *Ibid.*, **42**, 336 (1902). *J. Am. Chem. Soc.*, **24**, 1141 (1902).
[5] *Am. Chem. J.*, **35**, 432 (1906).
[6] *J. Am. Chem. Soc.*, **30**, 68 (1908).

Dividing these simultaneous equations by each other, we obtain

$$\frac{C_A}{C_C} = \frac{S_1^2}{S_2^2};$$

the ratio of the concentrations of those ions which are not common to both salts is the ratio of the squares of the solubilities of the two salts. From this interesting relationship it becomes possible to calculate the concentrations of ions which can be in equilibrium with two such salts, or, having determined the concentrations of the ions by analysis, to calculate the relative solubility of the two insoluble salts; such calculations have given values in good agreement with the experimental figures.

If equilibria be considered in which the two salts present have no ion in common, the treatment is essentially that used for the common ion effect, extended so as to include the larger number of molecular species present. Let the relatively insoluble salt AB be treated in solution with a known amount of CD; the equilibrium is

$$AB + CD \rightleftharpoons AD + CB,$$

and in the solution there are four species of ions and four species of undissociated molecules; in addition to these eight unknowns, there is to be added the total solubility (m) of the salt AB which it is desired to calculate. The necessary nine equations are of the type previously outlined; four are simple linear equations expressing m and n in terms of ionic and molecular concentrations, three are dilution formulas for the three salts CD, AD and CB, and the remaining two express the constancy of the solubility product $A \times B$ and the constancy of the molecular solubility. Using this basis of calculation, it follows at once that any salt will have its solubility increased by the addition of any second salt possessing no ion in common; and that the increase in solubility will be greater when AD or CB is a weak compound (or when both are weak). Noyes[1] has tested a number of such cases with satisfactory results. The solubility of a salt of a weak acid in a solution of a strong acid is given in Table XXXV; this type of reaction has been found generally to give a fairly close agreement between calculated and experimental results.

TABLE XXXV

SOLUBILITY OF SILVER BENZOATE IN NITRIC ACID

Conc. of HNO_3	Solubility Found	Solubility Calculated	Percentage Difference
0.00	0.01144	—	—
0.004435	0.01395	0.01406	+ 0.78
0.008870	0.01698	0.01703	+ 0.29
0.008915	0.01715	0.01706	− 0.53
0.01774	0.02324	0.02390	+ 2.76
0.01783	0.02351	0.02396	+ 1.89
0.02674	0.03071	0.03159	+ 2.79

Critique of the Solubility Principles: Experimental work such as the foregoing has naturally led to a general adoption of the principles of Nernst and Noyes in discussion of solubility relations, where they have proved of great value. It has appeared, however, in the course of later investigations that, while the principles have usefulness, they are far from being quantitatively exact. It was Arrhenius[1] who first demonstrated that the principle of constant molecular solubility could not be rigorously maintained. It is a simple corollary of the principle that sufficient addition of a salt with an ion in common with the saturating salt may depress the ionic solubility (A of equation 1) to a quantity approaching zero, but the total solubility, by the same equation, should never become less than the molecular solubility a. Arrhenius detected in some of the experimental work of Noyes a case in which the total solubility had been depressed below this value by addition of a salt with a common ion, and on trial found that the same result could be attained in other cases as well; Table XXXVI shows the data for two out of several silver salts upon addition of the corresponding sodium salt.

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[1] Noyes, *Z. physik. Chem.*, **27**, 267 (1897); Noyes and Schwartz, *ibid.*, **27**, 279 (1898) *J. Am. Chem. Soc.*, **20**, 742 (1898); Noyes and Chapin, *ibid.*, **20**, 751 (1898).

TABLE XXXVI

SOLUBILITY OF SILVER SALTS

Total Solubility Ag-Butyrate	Na Butyrate Added	Molecular Solubility	Total Solubility of Ag Acetate	Na-Acetate Added	Molecular Solubility
0.0224	0	0.0042	0.0594	0	0166
0.0027	0.493	- -	0.0147	0.50	

In the above examples it will be seen that addition of the sodium salt up to about 0.5 normality has in each case lowered the total solubility of the silver salt to less than the solubility of its undissociated molecules, which of course is a direct disproof of the principle of the constant molecular solubility. It will be seen that this demonstration involves no assumptions other than equation 1 (which cannot be attacked without denying the essential validity of the whole theory of electrolytic dissociation), and as a second assumption that the value of the molecular solubility is as given by measurements of electrical conductivity. Should these latter figures be in error, however, by any moderate amount only, the conclusion of Arrhenius would nevertheless be valid namely, that the molecular solubility is not a constant. It is therefore impossible to maintain the accuracy of Nernst's first principle in the face of this evidence, although it is doubtless true that the decrease in the molecular solubility is not great where the concentration of the second salt is kept small.

At a later date it was shown that Nernst's second principle, that of the constant solubility product, is also to be looked upon simply as a first approximation, and not as quantitatively true. The tests of this second principle have been made along two different lines and have led to different conclusions as to the direction in which the deviation from constancy occurs.

Hill[2] found that in a limited number of instances the treatment of a saturated solution with additions of a second salt having no ion in common with the first resulted in a decrease in solubility instead of the increase demanded by the theory, and that this decrease could be carried on sufficiently far so as to permit a process of reasoning like that used by Arrhenius in his demonstration of the untenability of the first solubility principle. The argument is as follows: let the salts AB and CD (of which AB is the saturating salt) be in equilibrium, and let A, B, C and D represent the four ionic concentrations and a, b, c and d the four molecular concentrations:

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[1] *Z. physik. Chem.*, **31**, 197 (1899).

[2] Hill, *J. Am. Chem. Soc.*, **32**, 1186 (1910); *ibid.*, **39**, 218 (1917).

$$\underset{a}{AB} + \underset{b}{CD} \rightleftarrows \underset{c}{AD} + \underset{d}{CB},$$

then, writing two equations to represent the solubility m of AB at equilibrium,

$$(1)\quad m = A + a + c,$$
$$(2)\quad m = B + a + d,$$

and by the principle of the constant solubility product, which is to be tested,

$$(3)\quad A \times B = K.$$

Multiplying (1) by (2) and extracting the square root,

$$(4)\quad m = \sqrt{A \times B} + x,$$

where x is used to indicate the various other terms, all of which have positive values; now substituting from (3),

$$(5)\quad m = \sqrt{K} + x$$

which indicates that, on the assumption of the constant solubility product, the total solubility can never be less than the value $\sqrt{K}$. In Table XXXVII are shown cases which were tested.

TABLE XXXVII

SOLUBILITY IN MILLI-EQUIVALENTS PER LITER

Conc. of Soluble Electrolyte Added	$AgBrO_3$ in $HC_2H_3O_2$	$(CH_3)_4NI$ in KOH	$(CH_3)_4NI$ in NH_4OH	$TlCl$ in $HC_2H_3O_2$	$PbCl_2$ in $HC_2H_3O_2$
0.00 N......	8.2668	262.28	262.28	16.085	77.53
0.20 N......	8.1451	252.00	261.8	15.82	77.03
0.50 N......	7.9041	237.7	261.5	15.29	73.40
1.00 N.......	7.6392	204.6	260.6	14.73	67.00
2.00 N.....	6.75	139.4	258.8	13.03	54.30
3.68 N	—	—	—	—	37.88
$\sqrt{AB}$	7.73	167.8	167.8	14.32	42.50

In four of these five cases the total solubility has become less, upon addition of a soluble electrolyte, than the value $\sqrt{K}$, and it is therefore clear that not only has the solubility product varied in its value, but that it has been decreasing with an increase in the total concentration. While the conclusion does not seem to be open to criticism for the cases given, it cannot of course be proven that the variation in the solubility product is always in this direction.

Taking the more usual cases in which the total solubility increases upon addition of the second electrolyte, Noyes, Bray, Harkins and others[1] have likewise deduced that the solubility product varies but that there is an increase in its value with increasing total concentration. In testing the principle for a large number of typical cases, eight equations have been used, of which four define the concentrations of the two salts taken in terms of their molecules and ions, and the remaining four are dilution formulas modified in accordance with Arrhenius's isohydric principles. Taking the solubility found as a known term, there are therefore only eight unknowns—the concentrations of the four molecular compounds and of the four ions, and the number of equations is sufficient therefore for a calculation of all concentrations, from which conclusions can be drawn both as to the solubility product and as to the molecular solubility. Measurements of the electrical conductivity of the solutions at equilibrium were in good agreement with the conductivity calculated from the ionic concentrations found. Cases where common ions are present required a smaller number of equations, and were treated by the same method. The results for one such case follow.

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[1] Noyes and Bray, *J. Am. Chem. Soc.*, **33**, 1643 (1911); Noyes, Boggs, Farrell and Stewart, *ibid.*, **33**, 1650 (1911); Bray and Winninghoff, *ibid.*, **33**, 1663 (1911); Bray, *ibid.*, **33**, 1673 (1911); Harkins, *ibid.*, **33**, 1807 (1911); Harkins and Winninghoff, *ibid.*, **33**, 1827 (1911); Harkins, *ibid.*, **33**, 1836 (1911).

TABLE XXXVIII

SOLUBILITY OF TlCl IN KCl SOLUTIONS IN MILLI EQUIVALENTS PER LITER

Added KCl	Total Solubility of TlCl	Conc. $\overset{+}{K}$	Conc. $\overset{+}{Tl}$	Conc. $\overset{-}{Cl}$	Conc. KCl	Conc. TlCl	$\overset{+}{Tl} \times \overset{-}{Cl}$
0.0 ..	16.07	0.0	14.32	14.32	0.0	1.755	204.9
25.0 ..	8.69	22.58	7.30	29.88	2.42	1.390	218.1
50.0 . .	5.90	44.15	4.70	48.85	5.85	1.204	229.6
100.0 ...	3.96	85.5	2.90	88.40	14.5	1.061	256.3
200.0 .	2.68	164.8	1.74	166.54	35.2	0.94	290.0

The figures of the seventh column show that the molecular concentration of undissociated TlCl decreases with increasing total concentration, as previously shown by Arrhenius, while the last column shows that the solubility product is far from a constant, and increases in value with increasing total concentration, similar results were found for a large number of cases. It has been pointed out, however,[1] that the conclusion assumes the quantitative validity of the dilution formula used in the calculations, and that with sufficient change in the dilution formula used the solubility product may be calculated as either increasing, decreasing or remaining constant with changes in the total concentration. Until certainty can be arrived at with respect to the formula expressing the change of ionization of a single salt with changes of concentration, it is clear that calculations based upon such a formula are open to the possibility of error.

It appears from the foregoing that the solubility principles of Nernst may properly be used only as first approximations, with which restriction, however, they are extremely useful. The molecular solubility has been shown to be no true constant, but to decrease with the total concentration present; the solubility product is no true constant, but decreases or increases with the concentration, possibly dependent on the nature of the substances; and the dilution formulas, as shown in the chapter on electrolytic dissociation, are doubtless far from telling us the exact degree of dissociation of the electrolytes present. It should be kept in mind however that probably all three of these principles approach more nearly to the truth as the concentration of the solutions becomes extremely small, and that probably our calculations for the solubility of very insoluble salts in presence of small amounts of a second electrolyte are quite close to the truth.

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[1] Hill, *J. Am. Chem. Soc.*, **39**, 230 (1917).

Recently Brönsted[1] has proposed a treatment of the solubility relations of electrolytes on a thermodynamical basis. The reader is referred for details to a later chapter (chapter XII) where the activity concept is developed.

THE THERMODYNAMICS OF HETEROGENEOUS EQUILIBRIA[2]

The position of equilibrium of a given process in one phase may be referred to that obtaining in another phase by application of the distribution law to the individual components of the process in the two phases. Consider the general case of a reaction proceeding in the vapor phase and simultaneously in the liquid condition. Let the reaction be generalized by the equation

$$aA + bB = cC + dD.$$

From the thermodynamic reasoning given in the preceding chapter the respective equilibria in the two phases are, in the gas phase

$$K_P = \frac{P_C{}^c \times P_D{}^d}{P_A{}^a \times P_B{}^b}$$

and in the liquid phase

$$K_X = \frac{X_C{}^c \times X_D{}^d}{X_A{}^a \times X_B{}^b},$$

where P and X refer to the respective partial pressures and mol. fractions. The relations between the various quantities in the two equations are connected by means of expressions, based upon the distribution law, of the form

$$P_A = k_1 X_A; \qquad P_B = k_2 X_B; \qquad P_C = k_3 X_C; \qquad P_D = k_4 X_D.$$

It therefore follows that

$$K_P = K_X \frac{k_3{}^c \times k_4{}^d}{k_1{}^a \times k_2{}^b}.$$

An example of this type has recently been studied by Edgar and Schuyler[3] in the esterification equilibrium. The equations given imply that the solution has the properties of a perfect solution. Where this does not hold the equations become more complex as outlined in the first section of this chapter.

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[1] Brönsted, *J. Am. Chem. Soc.*, **42**, 761 (1920); *ibid.*, **42**, 1478 (1920); *ibid.*, **43**, 2265 (1921); *ibid.*, **44**, 877 (1922); *ibid.*, **44**, 938 (1922).

[2] Contributed by the Editor.

[3] *J. Am. Chem. Soc.*, **46**, 64 (1924).

The equilibrium, K_X', in one solvent can similarly be related to the equilibrium, K_X, in another solvent by means of the partition coefficients of the respective molecular species between the two solvents.

Gas-Solid Equilibria: In the case of heterogeneous reactions, for example, between gases and solids, a knowledge of the saturated vapor pressure of the solid constituents enables one to refer the reaction to that taking place in the homogeneous gas phase. A simple typical heterogeneous reaction may be used by way of illustration, the oxidation of sulphur to sulphur dioxide. This reaction may occur either as a heterogeneous reaction between solid sulphur and oxygen or as a homogeneous process between sulphur vapor and oxygen. For the latter, it is evident that

$$K_P = \frac{P_{SO_2}}{P_S \times P_{O_2}}.$$

In the heterogeneous system with solid sulphur continuously present it is apparent that the partial pressure of the sulphur will remain constant throughout the reaction process and be equal to π_S, the saturated vapor pressure of sulphur at the given temperature. The equilibrium constant of the heterogeneous reaction will therefore be

$$K_P = \frac{P_{SO_2}}{P_{O_2} \times \pi_S}$$

or since π_S is constant at constant temperature,

$$\frac{P_{SO_2}}{P_{O_2}} = K_P \times \pi_S = K_P'.$$

It is therefore evident that the equilibrium condition for heterogeneous reactions, K_P', can be deduced by inserting the partial pressures (or concentrations, activities, etc.) of the reactants, present only in the gaseous phase, in the mass action relationship. The solid phases present influence the numerical value of the equilibrium constant.

The variation of this constant with temperature can similarly be associated with the variation of the equlibrium constant of the homogeneous reaction with temperature. In the example cited

$$K_P \text{ (homogeneous)} = \frac{K_P' \text{ (heterogeneous)}}{\pi_S}$$

or

$$K_P \cdot \pi_S = K_P'.$$

Now, from the discussion in the preceding chapter,

$$\frac{d\ln K}{dT} = -\frac{Q}{RT^2},$$

and, from the Clapeyron-Clausius equation,

$$\frac{dln\pi_S}{dT} = \frac{\lambda_S}{RT^2},$$

where λ_S is the latent heat of vaporization of solid sulphur. Hence,

$$\frac{dlnK_P \cdot \pi_S}{dT} = \frac{dlnK_P'}{dT} = -\frac{Q_P - \lambda_S}{RT^2} = -\frac{Q_P'}{RT^2}.$$

The quantity, Q_P', is the calorimetrically determined heat of reaction between solid sulphur and oxygen to form sulphur dioxide. The variation of K_P' with temperature is similar to that obtaining in the homogeneous system. For short intervals of temperature over which Q' may be regarded as constant the integrated form may be employed.

$$ln\frac{K_1'}{K_2'} = \frac{Q'}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right).$$

If we express Q_P, as in the preceding chapter, in terms of temperature by means of the equation

$$Q_P = Q_0 - qT - \tfrac{1}{2}rT^2 - \tfrac{1}{3}sT^3,$$

it follows that (see page 310)

$$lnK_P = \frac{Q_0}{RT} + \frac{q}{R}lnT + \frac{1}{2}\frac{r}{R}T + \frac{1}{6}\frac{s}{R}T^2 + \cdots + C.$$

In a similar manner, the vapor pressure may be expressed by an equation

$$ln\pi_S = -\frac{\lambda_{0(S)}}{RT} + \frac{k}{R}lnT + \frac{1}{2}\frac{m}{R}T + \frac{1}{6}\frac{n}{R}T^2 + \cdots + C_S,$$

whence it follows that

$$lnK_P' = \frac{Q_0 - \lambda_0}{RT} + \frac{q + k}{R}lnT + \frac{1}{2}\frac{r + m}{R}T + \frac{1}{6}\frac{n + s}{R}T^2 + \cdots + C',$$

where

$$C' = C + C_S.$$

Reference to the preceding chapter will indicate the nature of the magnitudes, q, r, s, $\cdots$. They are the algebraic summations of the m, n, o terms in the equations for the specific heats of the respective substances. For example, when

$$C_P = m + nT + oT^2 + \cdots,$$

we have, in the homogeneous reaction under consideration,

$$-\frac{dQ_P}{dT} = \Delta C_P = (m_{SO_2} - m_S - m_{O_2}) + (n_{SO_2} - n_S - n_{O_2})T$$
$$+ (o_{SO_2} - o_S - o_{O_2})T^2 + \cdots,$$

whence

$$\sum m = q; \qquad \sum n = r; \qquad \sum o = s.$$

In the expression for $ln\ \pi_S$ given above the quantity

$$ln\pi_S = -\frac{\lambda_0}{RT} + \frac{m_S - m_S'}{R} lnT + \frac{1}{2}\frac{n_S - n_S'}{R} T + \cdots + C_S,$$

where m_S, n_S, etc., refer to the respective terms in the expression for the heat capacity of the gaseous form, m_S', n_S', etc., refer to the corresponding quantities in the heat capacity of the solid substance. Hence, it follows that

$$lnK_P' = \frac{Q_0 - \lambda_0}{RT} + \frac{m_{SO_2} - m_{O_2} + m_S'}{R} lnT$$
$$+ \frac{1}{2}\frac{n_{SO_2} - n_{O_2} + n_S'}{R} T + \cdots + C'.$$

For a condensed system, solid or liquid, m' is the heat capacity at the absolute zero, and is, therefore, equal to zero, as specific heat measurements at low temperatures have shown. The equation therefore becomes

$$lnK_P' = \frac{Q_0'}{RT} + \frac{m_{SO_2} - m_{O_2}}{R} lnT + \frac{1}{2}\frac{n_{SO_2} - n_{O_2} + n_S'}{R} T + \cdots + C',$$

where Q_0' is the heat of the heterogeneous reaction at 0° K. In seeking a general solution for such equations and for the corresponding equations for homogeneous equilibria, Nernst suggested that the heat capacity of gaseous systems might be expressed by an equation of the form

$$C_P = a + 2\beta T + R = 3.5 + 2\beta T$$

with a corresponding equation for condensed systems of the form

$$[C_P] = 2\beta' T.$$

This latter is certainly incorrect at low temperatures. In many cases, however, the resulting equation for lnK_P' has been of great utility.

$$lnK_P' = \frac{Q_0}{RT} + \sum\nu 1.75 lnT + \frac{\sum\beta}{R} T + \cdots + \sum\nu I.$$

In its more usual form, as an approximation, this gives

$$\log K_P' = \frac{Q_P'}{4.58T} + \sum\nu 1.75 \log T + \sum\nu C,$$

where the $\sum\nu$ refers to the algebraic summation of the components, resultants positive, reactants negative, existing in the gaseous state alone, C to the integration constants of the vapor pressure equation, employing common logarithms, for the substances existing only as gases in the reaction process, the so-called Conventional Chemical Constants of Nernst.

The Nernst school has normally employed the approximation equation for homogeneous equilibria in the form

$$\log K_P = -\frac{Q_P}{4.571T} + \sum\nu 1.75 \log T + \sum\nu C,$$

and, for heterogeneous equilibria,

$$\log K_P' = -\frac{Q_P'}{4.571T} + \sum\nu 1.75 \log T + \sum\nu C.$$

In these cases K_P and K_P' are defined as $\frac{P_{(\text{reactants})}}{P_{(\text{resultants})}}$, $\sum\nu$ is defined as the algebraic summation of the molecular coefficients of the *gaseous* constituents, reactants positive, resultants negative; $\sum\nu C$ is defined as the algebraic sum of the chemical constants of the *gaseous* constituents, multiplied by the respective molecular coefficients, reactants positive, resultants negative. Thus, in the reaction,

$$CaO + CO_2 = CaCO_3 + Q_P',$$

$$\log K_P' = \log P_{CO_2} = -\frac{Q_P'}{4.57T} + 1.75 \log T + C_{CO_2}.$$

The following are some of the principal values employed by Nernst and his students for the conventional chemical constants.

H_2	1.6	HCl	3.0	N_2O	3.3	CH_4	2.8
N_2	2.6	HBr	3.2	NH_3	3.3	C_2H_6	2.6
O_2	2.8	HI	3.4	H_2O	3.6	C_2H_4	2.8
Cl_2	3.1	CO	3.5	H_2S	3.0	C_2H_2	3.2
Br_2	3.2	CO_2	3.2	CS_2	3.1	C_6H_6	3.0
I_2	3.9	NO	3.5	SO_2	3.3	CCl_4	3.4

The Dissociation of Silver Oxide: This dissociation has been measured by Lewis[1] in the lower range of pressures and by Keyes and Hara[2] over a much wider range. The data have been used by Pollitzer[3] to illustrate the use of the Nernst equation with numerical data shown in the following equation:

$$\log P_{O_2} = -\frac{13{,}130}{4.57T} + 1.75 \log T - \frac{0.010T}{4.57} + 2.8.$$

The agreement with the data of Lewis is shown in the following table.

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[1] *J. Am. Chem. Soc.*, **28**, 139, 158 (1906).

[2] *J. Am. Chem. Soc.*, **44**, 479 (1922).

[3] Die Berechnung Chemischen Affinitäten, Ahrens Sammlung, 17, 414 (1912).

TABLE XXXIX

P_{O_2} (atm.)	$T_{obs.}$	$T_{calc.}$
20.5	575	567
32.0	598	594
203.0	718	733

Lewis and Randall[1] express the experimental data by means of the equation

$$\frac{\Delta F}{T} = -RlnK = -\frac{7240}{T} - 1.0lnT + 21.95.$$

Gas-Liquid Reactions: The considerations given in the preceding section apply equally well to systems in which the condensed phase is a liquid. Here, also, the expression for K_P' contains the partial pressures of those constituents which appear in the gaseous phase only. Thus, in the reaction

$$2H_2O(g) + S(l) = 2H_2S(g) + SO_2(g),$$

the equilibrium constant

$$K_P' = \frac{P^2_{H_2S} \times P_{SO_2}}{P^2_{H_2O}}.$$

This reaction has been investigated by Randall[2] at the boiling point of sulphur. The mean value for K_P' at $T = 718°$ K. with the partial pressures expressed in atmospheres was 1.54×10^{-3}. The corresponding magnitude

$$\Delta F_{718} = -RTlnK_P' = 9240 \text{ cals.}$$

Equilibrium between a Solid and an Ideal Solution: The problem of equilibrium between solids and solutions is too complex to be treated adequately at this stage. A comprehensive discussion of ionization and of thermodynamic concentration in solution must precede such an undertaking. This is deferred to subsequent chapters. It is possible, however, to consider the equilibria existing between a solid and an ideal solution of this solid in a suitable solvent. Such an equilibrium is of course an equilibrium between a solid phase and its saturated solution. The change of equilibrium with temperature and pressure is actually the change of solubility with these two variables. It may also be regarded as the freezing point equilibrium of a binary system whose constituents form an ideal solution.

The general equation for the variation of such an equilibrium with temperature is

$$\frac{dlnX_B}{dT} = \frac{L_B}{RT^2},$$

where X_B represents the mol. fraction of the substance B in the binary system AB, L_B is the latent heat of fusion of B at the given temperature, the substance B being that constituent whose pure crystals are in equilibrium with the solution. In ideal solutions there is no heat of mixing of liquids. For a small temperature range over which L_B may be regarded as constant this equation may be employed in the form

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[1] Thermodynamics, p. 481. McGraw-Hill (1923).

[2] Diss. (1912); Lewis and Randall, *J. Am. Chem. Soc.*, **40**, 362 (1918); Thermodynamics, p. 545. McGraw-Hill (1923).

$$ln \frac{X_B'}{X_B} = \frac{L_B}{R}\left(\frac{T' - T}{TT'}\right).$$

The equation in this form has been employed by Schröder[1] with good agreement between calculation and experiment. The temperature of the melting point of the pure constituent B is chosen as the temperature T' since under these conditions X_B' is equal to unity. Agreement between calculated and experimental values for L_B becomes, in such cases, a criterion of ideality. Since,

$$\frac{dL}{dT} = \Delta C_P,$$

where ΔC_P is the difference of the molal heat capacities of the substance in the liquid and crystalline states it follows that

$$L_{B(\Delta T)} = L_{B(O)} + \Delta C_P \cdot \Delta T,$$

where $L_{B(O)}$ is the molal heat of fusion at the freezing point of the pure substance B. Under such circumstances,

$$\frac{dlnX_B}{dT} = \frac{L_{B(O)} + \Delta C_P \cdot \Delta T}{RT^2}.$$

This is the general equation for the freezing point lowering of an ideal solution.

This method has also been used by Washburn and Read[2] in the systems benzene-naphthalene, benzene-diphenyl and naphthalene-diphenyl to calculate eutectic temperatures. Excellent agreement between such calculations and experimental observations shows that these systems approach closely to ideality. Johnston and his co-workers[3] have recently shown that the number of such ideal solutions is probably considerably greater than has been hitherto realized. They have shown, for example, that *o*-, *m*- and *p*-nitro-anilines form, in pairs, ideal binary mixtures. Not only may the binary eutectics be calculated, but the ternary eutectic may be calculated thermodynamically. Exact agreement between calculated and experimental solubilities is obtained and between calculated and experimental values for the heats of fusion of the respective compounds.

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[1] *Z. physik. Chem.*, 11, 449 (1893).

[2] *Proc. Nat. Acad. Sci.*, 1, 191 (1915).

[3] Dissertations, Yale University, 1923, 1924.

CHAPTER X

THE MEASURMENT OF ELECTRICAL ENERGY

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All measurements of electrical energy are based on a fundamental law discovered by Ohm in 1827. Ohm's law states that the current in any circuit depends upon two variables, the voltage and the resistance of the circuit. The current has been found to be directly proportional to the voltage and inversely proportional to the resistance. It may be expressed algebraically thus:

$$C = E/R.$$

Exhaustive experiments have shown that Ohm's law holds rigidly for all classes of conductors, so that for the measurement of electrical quantities it is only necessary to define the units and set up the standards. From the algebraic statement of the law it may be seen that the possession of any two of the three units defines the third. The units are based on the c.g.s. system and the electromagnetic relations of the current

The unit of resistance, the ohm, is based on the c.g.s. system and the electromagnetic units, and was defined by the Electrical Congress at Paris in 1881 as the resistance of a column of mercury one mm. in cross section and weighing 14.4 gms. at the melting point of ice. Under such conditions the length of the column is about 106.3 cm.

The resistance of a metal is very decidedly affected by slight traces of impurities and, as mercury may be more rigidly purified than other metals, it was chosen as the standard. Like all metals, it has a considerable temperature coefficient so that it has been necessary to control definitely the temperature at which the resistance is determined.

Certain alloys have been discovered which have practically no temperature coefficient for ordinary ranges of temperature (manganin and constantin). From these alloys practical resistances have been made and carefully standardized, or compared with the mercury ohm in national bureaus of standards in France, Germany, England and the United States. We have, therefore, most satisfactory and reliable working standards of resistance. Neither the units of current, the ampere, nor of electromotive force, the volt, can be handled in this way. Each one of these units has given rise to a great deal of experimentation and discussion as to accuracy and reproducibility.

Both the ampere and the volt are based upon another law as fundamental as Ohm's law, discovered by Faraday in 1833, which shows the relation between the current and the amount of chemical reaction that takes place when a current passes from a first class, or purely metallic conductor, to a second class, or electrolytic conductor.

Faraday's Laws of Electrolysis: As a result of the electromagnetic properties of the current, permitting adjustment by observation of the deflection of a galvanometer, it is possible to establish a constant and uniform current, which delivers exactly equal quantities of electricity in equal intervals of time. When such a current is passed through a suitable cell, it has been found to liberate exactly equal amounts of hydrogen in equal time intervals. This same relation holds for metals deposited from solutions or fused salts. From these facts the first part of Faraday's law may be deduced, namely, that the amount of chemical action caused by the current is exactly proportional to the amount of electricity that passes in the circuit. Faraday called this instrument a "volta-electrometer" or voltameter.

The relation just outlined is not the only one discovered by Faraday; for, working with his volta-electrometer in series with cells in which metals were deposited, he found that different amounts of the several metals were deposited for the same amount of electricity. For example: 57.9 gm. of tin were deposited for one gram of hydrogen liberated in the voltameter. This is the equivalent weight of tin, and the weights of the other metals deposited for one gram of hydrogen (the equivalent weight of hydrogen) were found to be the equivalent weights of the metals concerned. These facts led to the second part of Faraday's law—that one and the same current liberates equivalent amounts of the elements, or produces equivalent chemical changes at the electrodes.

Faraday fixed his attention on the decomposition of water, taking the volume of the gases evolved as a measure of the amount of electricity that passed through his voltameter. Experience has shown, however, that there are more suitable reactions for the purpose in view. For example, the weight of a metal deposited from a solution may be more precisely determined than the volume of gases liberated by a current. Silver deposited from a suitable solution, on account of its large equivalent weight, 107.88 grams, and its excellent physical qualities, has proved to be particularly adapted to the measurement of quantities of electricity.

The Silver Coulometer: An exceptional amount of research has been devoted to the silver voltameter, or coulombmeter.[1] The silver is usually deposited in a platinum bowl or cup from a silver nitrate solution, and the increase in weight of the dish due to the deposit of silver is determined. If the current used in depositing the silver is uniform and the time it flowed is noted, then the strength of the current is readily obtained from the relation of coulombs to the weight of silver deposited. In this way the coulometer becomes an ammeter. Due to the exceptional precision of electrical measurements, the coulometer has been subjected to searching investigations as to its reliability.

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[1] Coulombmeter is the instrument for measuring coulombs, and this name, proposed by Richards, seems more suitable than the historic term voltameter. The word is generally contracted to coulometer.

Faraday found that there were many secondary reactions at the electrodes which caused apparent exceptions to the exactness of his law, but exhaustive research which has been carried out since 1833 has proved it to be one of the most if not the most exact of our laws.

A very drastic test of the law as applied to different conducting media was performed by Richards,[1] in which silver was deposited from a fused salt at 260 degrees and by the same current from a salt solution at 20 degrees. Four experiments showed an agreement in the deposits of one part in 22,500, or well within the limits of errors of the experiment.

Helmholtz regarded polarization as a most sensitive test of electrolysis. The products of electrolysis tend to recombine and form a counter current which may be detected and measured. Helmholtz found that he could detect in that way the decomposition of as little as 1×10^{-11} gms. of water. From experiments along this line we are justified in concluding that no electricity can pass from a first to a second class conductor without a rigidly equivalent chemical reaction occurring.

Generally, a 15 percent solution of silver nitrate has been used in the bowl for coulometer work and in this solution a piece of pure silver serves as an anode. Pure silver does not dissolve quite completely electrolytically so that a number of small particles of silver detach themselves from the anode, and thus a certain amount of exceedingly finely divided silver, or slime, is left. In order to keep this slime from the deposit in the bowl, Rayleigh recommended enclosing the anode in filter paper. This brought the solution in contact with cellulose and the question arose of the possible effect of filter paper on the weight of the deposit obtained. This has received a great deal of attention.

The general result has been to direct attention to the purity of the electrolyte as a means of securing reproducible results. Richards and his co-workers, in particular, have advocated surrounding the anode with a cup of porous porcelain to retain the anode slime and to keep the anode liquid away from the cathode. They claim that the anode liquid caused an abnormal result. These effects have not been definitely settled. All these questions have been exhaustively investigated by Smith, Mather and Lowry.[2]

Another question which has received a great deal of attention is the amount and nature of the inclusions in the electrolytic silver. Evidently it has been shown that the deposit is not pure silver but contains small amounts of included water and silver nitrate. The amount would seem to be less than 0.01 percent. This question has been particularly considered by Vinal and Bovard,[3] who also point out that the most accurate value for the absolute electrochemical equivalent of silver is that recommended as the international standard, 1.11800 mg., making the value of the Faraday

$$F = 96{,}494.$$

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[1] *Proc. Am. Acad. Arts Sci.*, **38**, 413 (1902).

[2] *Proc. Roy. Soc.*, **207**, 546 (1908).

[3] *J. Am. Chem. Soc.*, **38**, 496 (1916)

If the amount of the impurity were constant, it would not matter from the standpoint of measuring the quantity of electricity. Evidently, from the exhaustive work of Smith, Mather and Lowry (*loc. cit.*) it is possible to prepare solutions of silver nitrate which yield deposits of silver reproducible in mass to 1 or 2 parts per 100,000.

The conclusions concerning the best method of conducting the determination of current by means of the silver coulometer are given by Rosa and Vinal.[1] The porous cup and the F. E. Smith forms of voltameter are the most satisfactory. Electrolyte of the highest possible purity is essential. If it is pure, the weight of deposit is independent of the size of the voltameter; if impure, it is larger with large voltameters (volume effect). The temperature coefficient is zero. If the electrolyte is pure, the inclusions within the deposit average 0.004 per cent of its weight. The proposed specifications are in part:

> The electrolyte shall contain 10 to 20 grams silver nitrate in 100 cc. of solution and shall be free from organic or other reducing substances and colloids as shown (1) by testing with 1 cc. of 0.001 *N.* $KMnO_4$ added to 10 cc. of 66 per cent silver nitrate solution acidified, (2) by yielding an unstriated deposit, (3) by absence of the volume effect. Silver nitrate is purified by crystallization from acid solution and fusion, repeatedly, if necessary. The voltameter should contain not less than 75 cc. in the cathode chamber and the concentration at the surface of the cathode should not be reduced during electrolysis below 5 per cent. The electrolyte should be neutral or but slightly acid (1 part in 1,000,000) as tested by methyl red (0.2 per cent in alcohol) or iodeosin (10 mg. per liter) in ether, after removal of the silver by neutral potassium chloride. The electrolyte must be neutral or slightly acid at the end of the experiment. The anode should be of pure silver and is preferably coated with electrolytic silver. It should have as large an active area as the instrument permits. The current should be constant and not more than 1 ampere for not less than 1 hour. After washing, the cathode bowls should be dried at 150° C.

The only other coulometer which has received careful study is the iodine coulometer.

The Iodine Coulometer: Washburn and Bates[2] have shown that an iodine coulometer is capable of a reproducibility of 0.002 per cent for the iodine liberated at the anode in a potassium iodide solution. In addition, the iodine surrounding the cathode in the potassium iodide solution disappears. The change in the amount of iodine at either electrode may be accurately measured by titration. It was shown that the change in the amount of iodine at the anode and the cathode checked to within three parts in a hundred thousand. This constitutes a unique check on the accuracy of the determination and the correctness of the assumed electrochemical reactions. The iodine coulometer as used by Washburn and Bates was directly compared with the silver coulometer used at the Bureau of Standards at Washington where so much exhaustive work has been done on the silver coulometer.[3] The silver deposited in the coulometer was directly compared with the iodide liberated by the same current and measured by titration, thus giving a direct comparison of the equivalent weights of iodine and silver, which, for these elements, should be the same as their atomic weights. The coulometer comparison gave the ratio of silver to iodine as 0.85017 while the best figure for the atomic weights by chemical methods appears to be 0.84998. The difference is well within experimental errors and constitutes a most satisfactory agreement between chemical and electrochemical values.

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[1] *Bull. Bur. Standards*, **13**, 479 (1916), *Sci. Paper 285.*

[2] *J. Am. Chem. Soc.*, **34**, 1341 (1912).

[3] *J. Am. Chem. Soc.*, **36**, 916 (1914), *Bur. of Standards, Sci. Paper 218.*

The Absolute Measurement of Current: All of this gives only a precise and reproducible method of measuring a current and must be compared with the value of the current in absolute or c g s. units From the electromagnetic action of the current the following convention has been agreed upon: In a conductor one cm. of which is in the form of an arc of one cm radius, the current which produces a force of one dyne on a unit magnetic pole at the center of this arc is defined as the electromagnetic unit of current. For practical purposes this is too large a unit, so the ampere commonly used is one tenth of the electromagnetic unit.

A conductor carrying a current behaves as a magnet If two coils in the form of helices are arranged co-axially, a current passing through them in series causes them to act on each other with a force which may be calculated in absolute or c.g.s. units, from a knowledge of the dimensions of the coils and the current employed. Or, if we know the force and the dimensions of the coils, the current may be calculated. If one coil is fixed and the other suspended from the beam of a balance, the force due to a given current may be measured in gravitational units. Such a current weigher has been constructed by Ayrton, Mather and Smith.[1] The following extracts from their paper will indicate the historical development and the use of this instrument

A current can be measured absolutely in the electromagnetic system of units either by means of the action of the current on a magnet or of the current on a current. The former method has the disadvantage that at least two independent measurements are necessary For example, in using an electromagnetic balance, the strength of the magnet acted on by the electric circuit has to be determined, as well as the force exerted on the magnet by the circuit. In galvanometers, either of the sine or tangent type, the magnetic field produced by the electric circuit is compared with the earth's horizontal field, the strength of which is determined independently. Further, as the strength of artificial magnets cannot be regarded as truly constant, and the earth's field is subject to diurnal and secular variations, this class of measurement is not ideal.

In the electrodynamic class of measurement the mutual action between two or more coils carrying current takes the form of a torque, as in electrodynamometers, or a direct force, as in current weighers. In electrodynamometers, the torque may be measured with a bifilar suspension, the torsion of a wire or spring, or by means of a gravity balance. Current weigher measurements are almost always made by direct comparison with gravity, which is believed to be constant, and is known to a higher degree of accuracy than the strengths of any magnet or magnetic field that has yet been measured.

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[1] *Proc. Roy Soc*, **207**, 464 (1908).

Shortly after the absolute system of units was devised by Gauss and Weber in 1832, A. Becquerel weighed the attraction between a coil and a magnet; and two years later Lenz and Jacob used and modified Becquerel's balance by arranging a coil and magnet at each end of the beam. In 1840 W. Weber determined the electrochemical equivalent of water, using the tangent galvanometer as his instrument for measuring current; and in 1843 similar measurements were made by Bunsen and by Casselmann, followed in 1851 by Joule.

Meanwhile W. Weber had, in 1846, invented his two forms of electrodynamometer, one with the suspended coil inside, and the other with this coil outside the fixed coil, and he measured the torque with bifilar and unifilar suspensions.

The first current weigher appears to have been constructed by Cazin in 1863. In 1864 Joule made a current weigher having three circular flat coils wound with copper strip, one being suspended from a balance, so that its mean plane, which was horizontal, was midway between those of the other two fixed coils. This instrument had the correction to its principal constant determined by comparison with a standard tangent galvanometer, and was employed in Joule's electrical determination of the mechanical equivalent of heat. Its object was to enable a constant current to be maintained through the calorimeter, independent of variations in the earth's magnetic field.

The subject attracted considerable attention from this time onward, as is evident from the researches of Latimer Clark,[1] Kohlrausch,[2] Mascart,[3] Lord Rayleigh[4] and Mrs. Sidgwick,[5] Gray,[6] Pallet and Potiers,[7] Heydweiller,[8] Kahle,[9] Jones and Ayrton.[10] More recent determinations are due to Paterson and Guthe[11] employing a torsion electrodynamometer and to Guthe[12] (1906) using a modified Gray electrodynamometer.

The current balance of Ayrton, Mather and Smith may now be described. The instrument consists of a very sensitive physical balance supporting a coil with vertical axis from each end of the beam, these coils hanging coaxially within fixed coils carried from the base of the balance. A diagrammatic sketch of the arrangement is shown in Fig. 1.

From the diagram it will be seen that the current flows in opposite directions in the upper and lower parts of the outer coils. On the left-hand side of Fig. 1 the current in the upper half of the outer coils flows clockwise (looking from above) and in the lower half counter-clockwise, whilst in the left-hand suspended coil the circulation is shown clockwise. The tendency is, therefore, to lift the suspended coil *SL*. It will also be seen that the outer coils on the right will tend to depress the suspended coil *SR*, so that the two sets of coils exert a clockwise torque on the beam. This torque is balanced by weights added to or taken from scale pans supported independently on the knife edges which carry the suspended coils, an arrangement which avoids displacement of the suspended coils when the weights are placed or removed.

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[1] *Proc. Roy. Soc.*, May 30, 1872; *Phil Trans*, 1874, Part I.

[2] *Pogg. Ann.*, **170** (1873).

[3] *Jour. de Phys.*, (2) **1**, 109 (1882).

[4] *B. A. Report*, p. 445 (1882).

[5] *Phil. Trans.*, 175, 411 (1884).

[6] *Phil. Mag.*, **22**, 339 (1886).

[7] *Jour. de Phys.*, VI, 175, and IX, 381 (1890).

[8] *Wied. Ann.*, **44**, 533 (1891).

[9] *Wied. Ann.*, **59**, 532 (1896).

[10] *B. A. Report*, Bristol, 157 (1898), *Jour. Inst. Elec. Eng.*, **35**, 12 (1905).

[11] *Phys. Rev.*, **7**, 257, 1898.

[12] *Phys. Rev.*, **9**, 288, 1899.

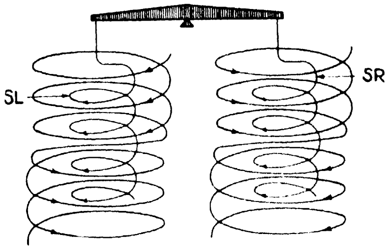

FIG. 1. Diagrammatic Illustration of Current Balance

All the coils are wound with bare wire on hollow marble cylinders, having double-threaded screw grooves cut on the surfaces, into which separate wires are laid as shown in Fig. 2. In this figure one wire is indicated by two thin lines, and the other is shown thick. The two wires, hereafter distinguished as No. 1 and No. 2, form two adjacent helices which, in the use of the instrument, are connected in series and act as one coil. They can, however, be readily disconnected from each other and an insulation test made between them. This applies to each of the six coils forming the current weigher, arrangements being made whereby the six No 1 wires may be connected together, the six No. 2 wires similarly grouped, and the insulation between adjacent wires of the whole instrument tested simultaneously. Any leakage between the two adjacent helices can thus be readily detected and localized and remedied.

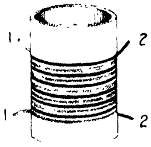

FIG. 2. Method of Winding Coils

Each of the fixed cylinders carries four helices, two upper and two lower, and each suspended cylinder two. There are therefore twelve helices in all, and these are connected in series, in the normal use of the current weigher, by means of small concentric cables running to a plug board and commutators outside the balance case. Flexible connections are used as leads and returns to and from the suspended coils. The commutators enable the direction of the current in any coil to be changed at will. By reversing the current in the coils on the fixed cylinders the forces between the fixed and suspended coils are reversed, and the apparent change of weight thus produced is a measure of the square of the current used.

The same current weigher was used by Smith, Mather and Lowry in their exhaustive investigation of the silver voltameter. They were thus able to measure their current in absolute units and concluded that their measurements and results were reliable to 2 parts in 100,000. They found that the ampere current deposited .00111827 gram of silver in one second. This is the amount of silver deposited by a coulomb—an ampere per second. Now, if we divide the equivalent weight of silver by their figure, $\frac{107.88}{.00111827} = 96{,}471$ coulombs per gram equivalent, which would be the same for the equivalent of any element or for any chemical reaction. This quantity is a fundamental constant of electrochemical action and is known as the Faraday.

Guthe *(loc. cit.)* summarizes the theory of the use of the electrodynamometer in these words: "As was first pointed out by Gray the expression for the torque between the two coils of an electrodynamometer assumes a simple form if the dimensions of both coils are chosen so that the length and the radius are in the proportion 3 : 1, if their centers coincide and, finally, if the dimensions of the fixed coil are large in comparison with those of the movable coil. Under these conditions the expression for the torque between the two coils with their axes at right angles to each other becomes

$$T = \frac{4\pi^2 N n r^2}{D^2 + L^2} I^2,$$

where N and n are the number of turns in the stationary and movable coils, D and L the diameter and length of the stationary, r the radius of the movable coil, and I the current, expressed in c.g.s. units."

Previously many determinations of the current have been made in absolute units and expressed in weight of silver per coulomb.

		Milligrams
Mascart	1884	1 1156
Kohlrausch	"	1.1183
Rayleigh and Sidgwick .	"	1.1179
Pallet and Potiers	1890	1.1192
Kahle	1899	1 1183
Paterson and Guthe	1898	1 1192
Pallet and Dedue	1903	1 1182
Guthe	1906	1.1182

These determinations were made by the use of the tangent galvanometer and the electrodynamometer. It appears therefore that our knowledge of the current in absolute units is satisfactorily known.

The Measurement of Electromotive Force: Congresses have defined the ampere as that unvarying current which deposits 0.001118 gram of silver per second in a coulometer of definite specifications. A perusal of the work done on the coulomb indicates that, for high precision, one must use exceptional facilities and great experimental ability. Attempts have therefore been made to develop units of electromotive force and with somewhat more favorable results from the standpoint of practical measurements, since standard cells may be constructed which are satisfactorily reproducible. A voltaic cell is a combination of metallic conductors or electrodes joined by an electrolyte and the possible reactions at the junctions of the electrolyte and metallic conductors furnish the electromotive force and the current. From the standpoint of thermodynamics a definite chemical reaction should give a definite electromotive force to the cell. It is, however, not only the purely chemical reactions which take place at the electrodes, but all other changes occurring that take part in the generation of current. For example, it would seem that two perfectly pure pieces of silver in a uniform silver nitrate solution should give zero potential and no current when joined externally, but this is not so, though the chemical reactions at the electrodes must be the same. It is generally found that two pieces of silver from the same pure silver wire show an electromotive force when opposed in any silver solution. Presumably, there are certain strains or physical differences which account for this, since annealing the electrodes causes the electromotive force to diminish markedly. Soft metals show better agreement than hard metals. Pure mercury electrodes show the best agreement, and amalgams are more satisfactory than metals in this respect. In general a liquid electrode is necessary where precision and reproducibility are required. The old Daniell cell, amalgamated zinc in zinc sulphate, copper sulphate, copper,

$$\mathrm{Zn\,Hg} \mid \mathrm{ZnSO_4\,aq} \mid \mathrm{CuSO_4\,aq.} \mid \mathrm{Cu},$$

was long a working standard, but it did not have the constancy or reproducibility demanded by the precision possible in electrical measurements. A much more reproducible and constant cell was proposed by Latimer Clark in 1872. The Clark cell was composed of a negative pole consisting of an amalgamated zinc electrode in a saturated zinc sulphate solution, and, for the positive pole, mercury covered with mercurous sulphate in zinc sulphate solution. The mercury constitutes a liquid electrode, and the zinc amalgam is also essentially a liquid electrode. Thus, many sources of irregularity were eliminated. This cell gave a voltage of 1.433 volts at 15 degrees, but diminished by about 0.001 volt per degree between 15 and 25 degrees. A rigid temperature control was therefore necessary. Edward Weston in 1892 found that, by replacing zinc by cadmium throughout, a cell was obtained with a temperature coefficient only about one thirtieth of that of the Clark cell. In fact, by replacing the crystals of cadmium sulphate and the saturated solution by an unsaturated solution of cadmium sulphate of a definite strength, an unsaturated cell of practically no temperature coefficient for ordinary temperatures was obtained. While this cell has not the reproducibility of the saturated cell, it is reasonably constant and may be calibrated and thus compared with manganin resistances as a working standard.

Like the coulometer, the standard cell has received a great deal of attention. The investigations have shown that the materials used in the cell and their assembling need very precise specifications. In the Clark cell the negative electrode seems to be perfectly reproducible and constant. Zinc amalgam, amalgamated zinc and pure zinc all seem to have the same potential in the zinc sulphate solution.[1] A 10 per cent amalgam has generally been employed with a fused-in platinum wire as contact. Fig. 3 shows the usual form (or H cell) provided with suitable lead wires soldered to the fused-in platinum wires. This cell may be immersed in an oil bath where the temperature remains constant and can be rigidly controlled.

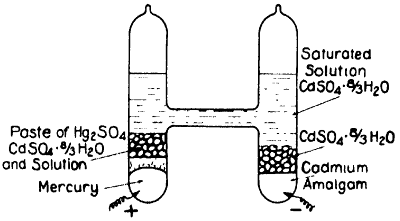

FIG. 3. Diagram of Weston Saturated Cadmium Cell

Freshly prepared cells were observed to have a higher electromotive force than seasoned cells from the same materials. The trouble was found to be in the cathode or mercury leg of the cell. Zinc sulphate is a very stable and reproducible salt, but this is not so with the mercurous sulphate used to cover the mercury as a depolarizer, for this salt readily hydrolyzes. In assembling the cell it was customary to wash mercurous sulphate with water, mix with zinc sulphate crystals and a saturated solution of zinc sulphate to form a paste. This procedure inevitably left some basic salt in the depolarizer and it was this salt which was responsible for giving the cell its initial high value. The first attempt to exclude the basic salt in preparing the mercurous sulphate and to exclude it in assembling the cell was made by Carhart and Hulett.[2] These precautions permitted the construction of cells which showed their normal electromotive force immediately a definite temperature was obtained. The cells also agreed among themselves to 1 part in 100,000. Equally satisfactory results were obtained with the cadmium or Weston cell.

The reproducibility of the standard cell invites a detailed consideration of the mechanism of the changes that take place in them when the current passes. In the Clark cell, the negative or zinc electrode is usually 10 per cent zinc amalgam which is a two-phase electrode, made up of zinc and saturated liquid amalgam which contains 2.22 per cent of zinc at 25°. It is this liquid amalgam which controls the potential of the electrode, as amalgams with less zinc give less potential, according to the Nernst logarithmic relation.[3] Evidently the two-phase amalgam adjusts itself to equilibrium very rapidly and exactly on change of temperature; so, this electrode is very reproducible and stable. The potential of the zinc electrode also varies with the concentration of the zinc sulphate in the electrolyte, but here again the solid zinc sulphate, $ZnSO_4.7H_2O$ maintains a saturated solution which also gives a definite, reproducible concentration for each temperature Nor does it appear that traces of impurities have a measurable effect on this electrical potential. The reaction that takes place on the passage of the current is the formation of $ZnSO_4$, and this is the main energy change in the cell. As will be subsequently discussed, the $ZnSO_4$ formed changes to the hydrate $ZnSO_4.7H_2O$.

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[1] See, however, Cohen and von Grimmeker, *Z. physik. Chem.*, **75**, 437 (1910).

[2] *Trans. Am. Electrochem. Soc.*, **5**, 59 (1904)

[3] *J. Phys. Chem.*, **14**, 158 (1910).

In the positive or cathode leg of the cell there is a solution saturated with respect to zinc sulphate and also with respect to mercurous sulphate in contact with the mercury electrode. The concentration of mercury ions in the electrolyte seems to be the controlling factor, so, attention has been directed to the purity of the mercurous sulphate which controls this concentration. The solubility is small, so that a slight variation in the purity or properties of the mercurous sulphate makes a measurable variation in the concentration of the mercury ions in the cathode leg and so in the voltage of the cell. The reaction that takes place at this electrode on the passage of the current is the decomposition of mercurous sulphate. A most precise and satisfactory insight into the workings of this cell has been formulated by means of a thermodynamical study.[1] Since the voltage in absolute units and the temperature coefficient are so accurately known, the Gibbs-Helmholtz relation is most suitably applied:

$$E = -\frac{\Delta H}{nF} + T\frac{dE}{dT},$$

where ΔH = the amount of heat energy absorbed, n = the valence and F = the Faraday.

In calculating the chemical energy by the use of this formula and the observed values of the cell a discrepancy of some 4000 cal. was found on assuming that the reactions were the formation of $ZnSO_4$ at the anode and the decomposition of Hg_2SO_4 at the cathode. However, one must consider that the $ZnSO_4$ formed at the anode was anhydrous and would interact with the solution, combining with the water to form $ZnSO_4.7H_2O$, and that removing water from the saturated solution would cause some of the salt to crystallize out. Both these changes are accompanied by marked thermal changes. When these were determined and taken into account, the agreement between the calculated and observed values was most satisfactory, so that our knowledge of the reaction at the electrodes in this cell is quite complete.

The Weston, or cadmium, cell is very similar to the Clark cell in many respects, but the cadmium amalgam used as the anode is not as simple as the zinc amalgam. It was found by Bijl[2] and Paschen[3] to be a much more complicated system. Cadmium amalgams of between 5 and 15 per cent of cadmium at ordinary temperatures consist of a liquid and a solid phase. The solid phase is not cadmium, but an isomorphous mixture of cadmium and mercury, which, however, has a very definite composition for each temperature and yields a very definite and reproducible liquid amalgam for any ordinary temperature. In fact, the potential of the usual 12 per cent cadmium amalgam against a saturated cadmium sulphate solution is most satisfactorily constant and reproducible. Tests on old cells which have changed in voltage have always shown that the amalgam potentials were entirely normal. The anode potential depends upon the concentration of mercury ions in a saturated cadmium sulphate solution surrounding the mercury anode and this has been found to be a complicated system. The main reactions in the Weston cell are the formation of $CdSO_4$ at the anode and the decomposition of the Hg_2SO_4 at the cathode, and the difference in the heats of these two reactions furnishes the bulk of energy of the cell. Profiting from the experience with the Clark cell, one must consider that the anhydrous cadmium sulphate formed at the anode will remove water from the saturated cadmium sulphate solution and cause a crystallization of some $CdSO_4.8/3H_2O$. Both of these changes are accompanied by measurable thermal changes and contribute to the energy of the cell. These heat reactions were taken into consideration by Cohen[1] but even then the agreement between the sum of all these heat changes and the electrical energy was unsatisfactory. The calculations had been based on the heat of formation of cadmium sulphate from metallic cadmium. But, in the cell, the cadmium sulphate is formed from cadmium amalgam and it was shown that some energy is required to remove cadmium from the amalgam. For, the potential between cadmium and cadmium amalgam opposed to each other in a cadmium sulphate solution is considerable. By using the potential of such a cell and its temperature coefficient it was possible to allow for this energy difference which was over 5000 cal. The agreement between the thermal data and the electrical energy of the cell was then most satisfactory. Here again therefore the thermodynamic treatment has given a clear insight into all the changes that take place in the cell. In the Clark cell, the amalgam has the same potential against a zinc sulphate solution as has pure zinc, so there is no correction needed for this factor in calculating the energy of the Clark cell.

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[1] E. Cohen, *Z. physik. Chem.*, **54**, 62 (1900).

[2] *Z. physik. Chem.*, **41**, 641 (1902).

[3] *Z. anorg. Chem.*, **36**, 201 (1903).

Many other combinations have been considered for standards of electromotive force, but nothing has been found to compare in reproducibility or constancy with zinc or cadmium cells. It has been pointed out that metals in the solid state are not suitable for constant electrodes, so that mercury is pre-eminently fitted to be one of the electrodes in a standard cell and a liquid amalgam must form the other. In order to secure sufficient voltage, the base metal chosen must be as far removed as possible from mercury in the voltaic series. It should also exist only in one stable state of oxidation. The metals that best satisfy these conditions are zinc and cadmium. The depolarizer which covers the mercury must be a salt of mercury. It should not have too great a solubility, and must be well defined physically and chemically, so as to yield a rigidly definite concentration for each temperature. Of the salts of mercury, mercurous sulphate seems most nearly to meet these requirements. If the depolarizer is a sulphate, the salt of the base metal which furnishes the solution must also be a sulphate. It therefore appears that the choices are decidedly limited and it seems improbable that other combinations as suitable as the Clark or the cadmium cell will be found. These two cells have shown a reproducibility of one part in ten thousand and there is some evidence to show that the Clark cell is the more constant of the two. The cadmium cell has shown more tendency to change with time, some cells of every set decreasing to low values and becoming useless as standards. An extended investigation[1] of this phenomenon showed that some chemical change, probably a slow hydrolysis of the mercurous sulphate, takes place in the cadmium sulphate solution. It appears to be a very slow reaction, though probably more rapid at the mercury electrode and surfaces. The essential facts are that if the content of the cathode system of the cell, Hg_2SO_4, hydrated cadmium sulphate, saturated solution and mercury, be thoroughly stirred, the voltage of the cell increases by about two millivolts. If the solids are now allowed to settle on the mercury electrode, the voltage of the cell decreases slowly with time, but does not stop at the value ordinarily obtained for the cadmium cells, but decreases to much lower values. The Clark cell seems to be quite free from these defects. It therefore seems probable that cadmium sulphate slowly hydrolyzes the mercurous sulphate and equilibrium is not obtained in the cathode system of the cell. However, a set of cadmium sulphate cells made with proper precautions should agree to one or two parts in 100,000, and many of these remain constant for years. It is necessary to make new sets at intervals as a check on the old cells. More work is needed to discover the exact nature of the changes which take place. A Clark cell while free from these defects has a much greater temperature coefficient and the cell shows a tendency for the glass to crack where the platinum lead wires are sealed in to make contact with the zinc amalgam. This cracking is presumably due to an alloying of zinc with platinum, resulting in a change of volume. This factor has generally ruined some cells of every set.

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[1] *Z. physik. Chem.*, **34**, 612 (1900).

International electrical congresses have devoted much attention to the cadmium or Weston standard cell on account of its low temperature coefficient and favorable characteristics. An important international conference was held in Washington at the National Bureau of Standards in 1910 with representatives from England, France and Germany present. Not only were the outstanding faults of the silver coulometer and the standard cells considered, but a considerable amount of experimental work was done on these problems and published in the Report to the International Committee on Electrical Units and Standards, Dept. of Commerce and Labor, Bureau of Standards, January 1, 1912. Specifications for the silver coulometer are considered and the value of the electromotive force of the Weston standard cell, as based on the coulometer, was given as 1.0183 volts at 20°. From investigations previously carried out and work done at the conference, a reproducibility of 1 or 2 parts in 100,000 would seem to be obtainable, although there are still outstanding problems of divergencies with both voltameter and the standard cell.

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[1] *Phys. Rev.*, **27**, 337 (1908).

The value of the electromotive force of standard cells in absolute units has been determined many times. The constant current has been determined by the electrodynamometer or the ampere balance, or has been based on the silver coulometer. When such a current passes over a known resistance there is a conventional fall of potential of 1 volt per ohm, the international volt being so defined and measured. The conventional value of the Weston cell was found to be 1.0183 volts at 20° and the change with temperature of these cells has been carefully determined by Wolf and Waters[1] as follows:

$$E_t = E_{20} - .0000406(t - 20) - .00000095(t - 20)^2 - .00000001(t - 20)^3.$$

For very precise work one must employ a thermostat capable of holding the temperature constant to 0.01°. As standard cells often take a considerable time (days) to attain their proper value at a given temperature, it is found necessary, for most precise work, to construct a number of cells and place them in a thermostat which would keep them constantly within 0.01° of a suitably chosen temperature. This is quite possible with modern thermostats[2] so that it is possible for the different laboratories to establish voltages which agree most satisfactorily. This is shown from the report of the meeting of the International Committee at Washington, 1910.

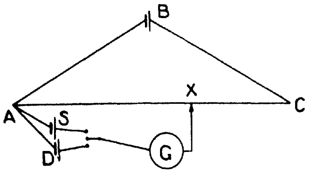

FIG. 4. Diagram of Pontentiometer Measurement

With this basis, precision measurements may be made of any other electrical quantities. The determination of voltage is accomplished by the zero, or Poggendorff method, where the standard cell is opposed to a fall of potential over known resistances (Fig. 4). The current from the battery, B, is passed over a resistance, AC; a shunt joined at A includes the cell and a sensitive galvanometer, G, and is joined to the resistance with a sliding contact, X, so that the electromotive force of the standard cell opposes the fall of potential over AX. The galvanometer, G, indicates the point at which there is a balance, and, if calibrated resistances are used, one knows the fall of potential over each ohm in the circuit. Supposing the cell is a Weston standard at 20° with an electromotive force of 1.01830 volts and one makes AX = 10,183 ohms, adjusting the resistance XC until balance is obtained; the potential fall over each ohm is exactly .0001 volt and it is readily seen that, using suitable resistances, such a method is capable of measuring voltages greater as well as less than the standard cell. The accuracy depends upon the accuracy of the resistances and the sensitiveness of the galvanometer. Perhaps no other physical measurements made are as accurate or satisfactory as those made by the compensa-

[1] *Bull. Bur. of Standards*, **5**, 309 (1908).

[2] *Phys. Rev.*, **32**, 276 (1911).

tion potentiometer method. It is a simple matter to measure accurately the voltage of any other cell by putting it in place of a standard cell, once the fall of potential has been determined. The Weston unsaturated cell is calibrated in this way, and then used as a working standard; it is, of course, necessary to maintain a steady and uniform current from the battery, *B*, through the circuit and this is tested from time to time by means of the standard cell.

CHAPTER XI

CONDUCTANCE, IONIZATION AND IONIC EQUILIBRIA

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Almost immediately after the discovery of the Voltaic pile,[1] Nicholson and Carlisle[2] decomposed water by a current from the pile passing between platinum and gold wires immersed in that liquid. Cruickshank[3] at the same time showed that metallic salts could be decomposed by the pile, and that during the decomposition of water the liquid became alkaline around one wire and acid around the other. This puzzling result was first explained by Humphry Davy,[4] who began experiments with the pile in 1800, and showed that decompositions could be effected in different vessels provided these were connected by strips of moist animal or vegetable substances, asbestos, or even the two hands of the experimenter.[5] In a careful research, carried out in 1806, Davy showed[4] that the acid and alkali were produced from impurities in the water, and that "water, chemically pure, is decomposed by electricity into gaseous matter alone, into oxygen and hydrogen." He found that[6] acids could be passed through alkaline solutions and *vice versâ*, and that apparently insoluble substances, when moist, were decomposed by the electric current. His experiments convinced him of the great decomposing power of the pile, and led to the isolation of the alkali metals. Davy never had any serious theory of the phenomena observed, and Faraday later on remarked[7] that "probably a dozen precise schemes of electrochemical action might be drawn up, differing essentially from each other, yet all agreeing with the statement there given" [by Davy].

After a period of mystification it became clear that voltaic electricity was fundamentally the same as frictional electricity, as had all along been maintained by Volta, and this was proved by experiments of Wollaston,[8] who showed that the effects produced by each were the same, and in particular that frictional electricity could produce chemical decomposition. Water had previously[1] been decomposed by sparks by van Trostwyk and Diemann, but in this case both gases were evolved from each electrode. In 1802 Erman[2] showed that the voltaic pile could affect a gold leaf electroscope. Any remaining doubts were set aside by an elaborate research by Faraday,[3] who realized clearly that the only difference between the effects produced by frictional and voltaic electricity was due to differences in quantity and intensity (voltage or potential). The frictional machine produced a very small quantity of electricity at high intensity, whilst the pile or battery produced a much larger quantity at a much lower intensity. The distinction between quantity and intensity, so fundamental in the study of electricity, was first made by Cavendish.[4]

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[1] *Phil. Trans.*, **90**, 403 (1800). Righi, Volta e la pila, Como, 1899

[2] *Nicholson's J.*, **4**, 179 (1800).

[3] *Ibid.*, **4**, 187 (1800); Henry, *ibid.*, **4**, 223 (1800)

[4] *Phil. Trans.*, **97**, 1 (1807); Works, ed. J. Davy, vol. 5, p. 1.

[5] *Nicholson's J.*, **4**, 294 (1800); Works, **2**, 139. *Phil. Trans.*, **91**, 397 (1801)

[6] *Phil. Trans.*, **97**, 1 (1807), Works, 5, 1

[7] *Phil. Trans.*, **123**, 684 (1833), Experimental Researches, Series 5, p. 136

[8] *Phil. Trans.*, **91**, 427 (1801)

Systematic researches on the decomposition of dissolved substances by the electric current were made by Hisinger and Berzelius in 1804.[5] They showed that acid or halogen always appeared at one pole, and alkali, metal, or hydrogen at the other. The products of decomposition appeared only at the poles.

Conductors and Non-Conductors: The distinction between conductors and non-conductors of electricity was first made experimentally by Stephen Grey[6] (1728–1736). The names were first used by Desaguliers in 1739.[7] Good conductors are metals, many sulphides such as galena and pyrites, aqueous solutions of acids, bases and salts, fused salts, and water when not perfectly pure. Bad conductors, or insulators, are dry solid salts, metallic oxides, ice, some metallic compounds, such as $SnCl_4$, $AsCl_3$, HgI_2, As_2S_2, and As_2S_3,[8] most non-metallic elements, pure water, most organic compounds, mica, and glass, all at the ordinary temperature. A large number of substances were examined and classified by Hampe.[9]

A curious relation between conducting power and optical properties was pointed out by Maxwell:[10] transparent substances are usually insulators. Light, according to Maxwell's theory, consists of electromagnetic energy, and if the substance through which it passes is a conductor, the electric displacements in the light wave generate electric currents in the material, which are dissipated as heat and thus the light is extinguished. Metals, which are opaque to light, are good conductors of electricity. In insulators, the electrons are bound and there are only displacements, not motion, of them, whereas in conductors the electrons actually move. Good metallic conductors are also good reflectors of light.[1] An apparent exception to the rule is exhibited by solutions of electrolytes, which are good conductors yet are transparent. In this case, however, the electricity moves in connection with material particles, the ions.

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[1] *Gren's J.*, 2, 130 (1790); cf. Strong, *Amer. Chem J.*, 50, 213 (1913).

[2] *Gilb. Ann.*, 11, 90 (1802).

[3] *Phil. Trans.*, 123, 23 (1833), Expt. Res., 3d Series, p. 76.

[4] *Phil. Trans.*, 66, 196 (1776), Collected Papers, ed. Maxwell and Larmor, Cambridge, 1921, vol. 1, p. 200.

[5] *Ann. Chim.*, 51, 167 (1804).

[6] Priestley, History of Electricity, 2d edit., London, 1769, p. 25.

[7] Priestley, *ibid.*, 62, on early history see J. C. Fischer, Geschichte der Physik, 8 vols., Göttingen, 1801–1808.

[8] Faraday, *Phil. Trans.*, 123, 507 (1833); Expt. Res., 4th Series, 110 ff., 7th Series, 201.

[9] *Chem. Z.*, 11, 54 (1887); 12, 1 (1888); Lorenz, Die Elektrolyse geschmolzener Salze, Halle, 1905–6; 3 parts; part 2, p. 182.

[10] Treatise on Electricity and Magnetism, Oxford, 1892, vol. 2, p. 446; Jeans, Electricity and Magnetism, Cambridge, 1911, 534.

Classes of Conductors: Early experimenters, such as Davy, noticed that conductors could be divided into two classes: (i) those in which the electricity moves without producing chemical changes; (ii) those in which chemical changes always accompany the passage of the current. Metals are typical of the first class, called *metallic conductors*. The second class comprises what are called, following Faraday,[2] *electrolytes*, or *electrolytic conductors*. Davy[3] noticed that the conductivity of metals diminishes with rise of temperature, whilst Ohm[4] found that of electrolytes to increase. Carbon is the principal exception to this rule: it conducts metallically but its conductivity increases rapidly with rise of temperature.[5] Silicon also shows this peculiarity.[6] Tellurium shows first an increase up to 70–80°, then a decrease, in conductivity with further rise in temperature.[7] The case of selenium, the resistance of which varies on exposure to light,[8] is well known. Some sulphides conduct metallically and others electrolytically, both solid and in the state of fusion. The latter increase in conductivity with rise of temperature.[9] Some peculiar results were noticed by Hittorf.[10] The conductivity of copper sulphide is increased by traces of free sulphur and the conductivity of the native sulphide depends on free copper. Silver sulphide appears to conduct metallically because of the formation of fine threads of silver. The supposed metallic conduction of fused silver halides is also due to threads of silver stretching from pole to pole.[11]

Unipolar Conduction: A peculiar class of conductors are those known as *unipolar*, which allow electricity to pass from one electrode only. Erman[12] noticed that if wires from a battery are introduced into a piece of dry soap no current passes. If the soap is connected to earth, current flows to earth from the negative wire only. The positive electrode becomes coated with an insulating layer of fatty acid. If the soap is moist, this is dissolved and current passes between the two wires.[1] The same phenomenon has been noticed in solutions, and whenever electrolysis leads to the formation of a sparingly soluble, poorly conducting, substance, which adheres to one of the electrodes, unipolar conduction occurs. This is applied in the aluminium rectifier,[2] which consists of a cell in which the anode is of aluminium and the electrolyte a solution of alkali phosphate, or borate, or a mixture of equivalent amounts of ammonium phosphate and borate. In this way an alternating is converted into a direct current.

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[1] N. R. Campbell, Modern Electrical Theory, Cambridge, 1913, 60.

[2] Expt. Res., 4th and 5th Series, p. 110, the nomenclature is introduced in Series 7, p. 197.

[3] *Phil. Trans.*, **111**, 431 (1821).

[4] *Ann. Physik*, **63**, 389 (1844).

[5] Cf. Muraoka, *Ann. Physik*, **13**, 307 (1881). S. P. Thompson, *Lumière électrique*, **22**, 621 (1886); Dewar and Fleming, *Phil. Mag.*, **34**, 326 (1892).

[6] Le Roy, *Compt. rend.*, **126**, 244 (1898). *Z. Elektrochem.*, **5**, 95 (1898).

[7] Exner, *Wien. Ber.*, **73**, 285 (1876). Lenher and Morgan, *J. Am. Chem. Soc.*, **22**, 28 (1900).

[8] Siemens, *Ann. Physik*, **159**, 117 (1876). Saunders, *J. Phys. Chem.*, **4**, 423 (1900).

[9] Faraday, Expt. Res., 1833, 4th Series, 110, 1838, 12th Series, 426, Karsten, *Ann. Physik*, **71**, 239 (1847); Beetz, *ibid.*, **92**, 452 (1854). Bellati and Lussana, *Atti R. Inst. Veneto*, **5**, 1117 (1888); Streintz, *Ann. Physik*, 190, 171 (1902); Abt, *ibid.*, **62**, 474 (1897); Braun, *ibid.*, **153**, 556 (1874), **1**, 95 (1877), **4**, 476 (1878), **19**, 340 (1883). H. Meyer, *Beibl. Ann. Physik*, **5**, 199, *Ann. Physik*, **19**, 70 (1883). Matteucci, *Compt. rend.*, **40**, 541 (1855); **42**, 1133 (1856).

[10] *Ann. Physik*, 84, 1 (1851). cf. Urazov, *J. Russ. Phys. Chem. Soc.*, **51**, 311 (1919).

[11] Le Blanc and Kerschbaum, *Z. Elektrochem.*, **16**, 680 (1910). See also following sections.

[12] *Gilbert's Ann.*, **11**, 149 (1802), **22**, 14 (1806), for unipolar conduction of flames see J. J. Thomson, Conduction of Electricity through Gases, Cambridge, 1906, chapter 9, and Becker, *Jahrb. Radioakt. Elektronik*, **13**, 139 (1916).

Theory of Metallic Conduction: Metallic conduction differs from electrolytic conduction in the following particulars:[3] (1) There are no products of electrolysis; (2) there is no polarization: solid electrolytes, e.g., barium sulphate, exhibit a polarization of over one volt; (3) a substance which dissolves in water without decomposition to give a solution containing ions will probably conduct electrolytically in the solid state; (4) the resistance of a pure solid conductor has a minimum value at some temperature, whilst that of an electrolyte always diminishes with rise of temperature; (5) selective absorption and emission in the ultraviolet and infra-red are exhibited by electrolytic conductors, whilst in the case of metallic conductors, absorption and emission are continuous.

The conductivities of some elements (e.g., Si and Ti) and compounds have been studied by Koenigsberger and Schilling,[4] who found that a maximum conductivity was reached at a particular temperature in each case, which has no connection with transition temperature, and is attributed to electronic dissociation. The conclusion that metals contain not only free electrons and positive ions, but also negative ions, was reached on theoretical grounds by Jaffé,[5] the negative ions being regarded as associations of electrons with neutral molecules. On the theory of metallic conduction now accepted, free electrons are supposed to carry the current, the positive ions of the metal being immobile, or practically so. Other results lead to this theory, such as the work of Tolman and Stewart,[1] who calculated the ratio of the effective mass of the current carriers to the quantity of electricity carried. This ratio indicates that the carriers are free negative electrons. The thermoionic emission from metallic wires at high temperatures is also in good agreement with the electron theory.[2]

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[1] The explanation given is due to Ohm.

[2] The rectifying action of aluminium was discovered by Buff, *Lieb. Ann*, **102**, 265 (1857). See also B. K. Norden, *Z. Elektrochem.*, **6**, 159, 188 (1899); F. Fischer, *Z. physik. Chem.*, **48**, 177 (1904); Roloff and Siede, *Z. Elektrochem.*, **12**, 670 (1906), other metals (Mg, Ta, Nb, Sb, Bi, Zn, Cd) Günther-Schulze, *Ann. Physik*, **21**, 929 (1906) (bibliography); **22**, 543 (1907); **23**, 226; **24**, 43; **25**, 775 (1908); **26**, 372; **28**, 787 (1909); **34**, 657 (1911), *Z. Elektrochem.*, **18**, 326 (1912); *Ann. Physik*, **41**, 593 (1913); Baborovsky, *Z. Elektrochem.*, **11**, 465 (1905); Kistiakowsky, *ibid.*, **14**, 113 (1908), Foerster, *Elektrochemie wässriger Lösungen*, 1915, 376 ff.; bibliography, Günther-Schulze, *Jahrb. Radioakt. Elektronik*, **17**, 356 (1921); Winther, *Phys. Z.*, **14**, 823 (1913) (Mg, Al, Zn, Cd, Fe, Co, Ni, Pb, Sn, Sb, Bi, Cu, Ag, Pt, Au, Cr in KOH Aq.); Weiser, *J. Phys. Chem.*, **22**, 77 (1918).

[3] Koenigsberger, *Z. Elektrochem.*, **15**, 97 (1909).

[4] *Ann. Physik*, **32**, 179 (1910); summary of recent work on metallic conduction, Meissner, *Jahrb. Radioakt. Elektronik*, **17**, 229 (1920). For detailed account see Graetz, Elektrizität und Magnetismus, Leipzig, 1923, Vol. 3, p. 597 (by Koenigsberger).

[5] *Physik. Z.*, **13**, 284 (1912); Kraus, *Phys. Rev.*, **4**, 159 (1914), concludes that only a small fraction of the molecules of liquid mercury are ionized.

An early attempt at a theory of metallic conduction was made by Riecke,[3] who assumed also positive mobile particles. In the theory of Drude[4] the electrons in a metal are assumed to have the same mean kinetic energy as a gas molecule at the same temperature, and collisions between electrons and between electrons and metal atoms occur in the same way as those between gas molecules. The conduction is explained by the directive effect of the applied E.M.F. on the motion of the electrons, which preserve their random motion unchanged. On these assumptions, with certain simplifications,[5] the conductivity of a metal can be shown to be given by:

$$\kappa = (e^2 N l)/(2\sqrt{2\alpha T m}),$$

where e = electronic charge, N = number of molecules per unit volume; l = path traversed by an electron between two successive collisions; T = absolute temperature; m = mass of electron; α is a constant given by the relation $\frac{1}{2}mv^2 = \alpha T$, where v is the velocity of the electron.[6] Thus:

$$\kappa = e^2 N l/2mv.$$

On the assumption of the classical kinetic theory we replace $\frac{1}{2}mv^2$ by $(3/2)kT$, where k is Boltzmann's constant, hence.

$$\kappa = e^2 N l v/4 \cdot \tfrac{1}{2}mv^2 = e^2 N l v/6kT.$$

By a similar calculation the coefficient of thermal conductivity is found to be given by:

$$\theta = \tfrac{1}{2} N k l v,$$

hence

$$\theta/\kappa = 3k^2 T/e^2 = T \times \text{const}.$$

which is the law of Wiedemann and Franz.[7]

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[1] *Phys. Rev.*, **8**, 97 (1916). **9**, 164 (1917).

[2] O. W. Richardson, The Emission of Electricity from Hot Bodies, London, 1916

[3] *Ann. Physik*, **66**, 353, 545 (1898).

[4] *Ann. Physik*, **1**, 566 (1900); **3**, 369 (1900), **7**, 687 (1902), the same theory was put forward independently by J. J. Thomson, Rapports du Congrès Internat., Paris, **3**, 138.

[5] Cf. Campbell, Modern Electrical Theory, 1913, p. 59

[6] Cf. Jeans, Electricity and Magnetism, 1911, p. 306; the velocity component due to the impressed E.M.F. is very small compared with the value of v. The value of N has been calculated from optical and thermoelectric constants. It is then practically independent of temperature. Cf. Schenck, Physikalische Chemie der Metalle, Halle, 1909.

[7] *Ann. Physik*, **89**, 497 (1853); L. Lorenz, *ibid.*, **13**, 422, 582 (1881), Kirchhoff and Hausemann, *ibid.*, **13**, 406 (1881), Jaeger and Diesselhorst, *Abh. d. phys. tech. Reichsanstalt*, **3**, 269 (1900); Lees, *Phil. Trans.*, **208**, 381 (1907).

The change of resistance with temperature is supposed by Schenck (*ibid.*) to be connected with the hardness of the metal.

Although experimental evidence on the whole supports Drude's theory, it is not free from difficulties. In the first place, the Wiedemann-Franz law is only approximate.[1] The experiments of Onnes at very low temperatures (see p. 493) show that a state of "super-conductivity" is reached before the absolute zero, when the resistance has practically vanished, and the resistance falls off more rapidly with temperature than according to the Wiedemann-Franz law. Again, the assumption of equipartition of energy between electrons and atoms would lead us to expect an additional $3/2 \cdot N_0 . k$, where N_0 is the number of electrons per gram atom, to the atomic heat of the metal, as compared with that of non-metals, which has never been observed. If we assume the number of electrons to be very small, the value of κ would be too small, unless l is given improbably large values.[2] Another serious difficulty is that the assumption of equipartition would lead to the result that metals should radiate according to the law of Rayleigh, whereas they actually follow Planck's law, especially at low temperatures (cf. Chapter XVI). Attempts to remove this difficulty have been made by Wereide[3] and Nicholson.[4] The latter points out that the assumption of equipartition enables the numbers of effective electrons in the atom to be calculated from the optical constants, and these come out very near whole numbers. This argument has very little weight, and it has been generally recognized that the theory of equipartition requires modification. Before discussing the newer theories brief mention must be made of the theory of Stark.[5]

In this the valence electrons are assumed to be distributed symmetrically between the network of positive nuclei, lying on displacement surfaces in which they can move freely under an applied P.D. The number of transportable electrons is independent of temperature and (in a univalent metal) equal to the number of atoms. At any given temperature the resistance is determined by the thermal vibration of the electric valency fields. The thermal vibration vanishes at the absolute zero, and there is then no resistance. The small conductivities of non-metals is explained by the assumption that only a small number of electrons lie on displacement surfaces. Reduction in conductivity caused by foreign materials is assumed to be due to disturbance of the symmetry in the displacement surfaces, brought about by a relatively small number of foreign atoms, the electrons and atomic spheres of which are assumed to have a different spacial arrangement. The valency electrons bind together the positive spheres, i.e., determine the cohesion, and Stark[6] has put forward evidence in support of the connection between conductivity and plasticity.

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[1] Lees, *Phil. Trans.*, **208**, 381 (1907); Meissner, *Ann. Physik*, **47**, 1001 (1915); cf. Lorentz, *Proc. Amsterdam Acad.*, 1905.

[2] C. F. Reiche, "Quantum Theory," Eng. transl. 1922, pp. 63 ff.

[3] *Ann. Physik*, **55**, 589 (1918).

[4] *Phil. Mag.*, **22**, 245 (1911); Schuster, *ibid.*, **7**, 151 (1904).

[5] *Jahrb. Radioakt. Elektronik*, **9**, 188 (1912); based on his valence hypothesis, *ibid.*, 124 (1908).

[6] *Phys. Z.*, **13**, 585 (1912), cf. Credner, *Z. physik. Chem.*, **82**, 457 (1913).

Wagner,[1] by comparing the conductivities of metals in the solid and liquid states, finds ratios varying from 0.5 to 4.0. The number of electrons being assumed constant, the change must be due to changes of mobility.

Among the newer theories which attempt to get over the difficulties before mentioned are those of Nernst,[2] Onnes,[3] Lindemann,[4] and J. J. Thomson.[5] The formula of Lindemann shows that at high temperatures the specific resistance is proportional to the absolute temperature, whilst at low temperatures it falls off proportionally to $e^{-h\nu/2kT}$, where h is Planck's constant and k is Boltzmann's constant = R/N_0. The existence of zero resistance at low temperatures is thus covered. Wien [6] discards the theory of equipartition of energy altogether and assumes that the electrons move with a velocity independent of temperature, and that N, the number of electrons per unit volume, is also independent of temperature. The variation of specific resistance is then determined only by the dependence of l, the mean free path, on temperature. Wien assumes a distribution of energy among the metal atoms in accordance with Debye's theory and finds

$$r = \text{const.} \times \int_0^{\nu_m} \frac{\nu d\nu}{e^{h\nu/kT} - 1} \quad (r = \text{specific resistance}).$$

In some respects this theory is at a disadvantage Thus, it does not lead to a theory of heat conduction without fresh assumptions.

More recently Lindemann [7] and Haber [8] have made the assumption that the electrons in a metal, instead of being free to move like atoms of gas, are bound together in a space lattice, which moves through the metal as a rigid structure. Two assumptions are made (1) at distances sensibly greater than the atomic radius electrons and ions (the parts of metal atoms from which electrons are removed) are attracted according to the inverse square law, whilst at distances less than a value a_0 they are repelled by a force $\lambda f(a)$, λ being a constant;[9] (2) N, the number of electrons per unit volume, D, the dielectric constant of the electrons, and λ, the constant of the repulsive force, are related by the equation

$$\phi(N, \lambda) \propto \psi(N, D),$$

where ϕ and ψ are unknown functions. This probably reduces to

$$N\lambda^{-1/2}D^{3/2} = \text{const.}$$

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[1] *Ann. Physik*, **33**, 1484 (1910).

[2] *Ber.*, **44**, 306 (1911).

[3] *Communications of Leyden Lab.*, 133 (1913).

[4] *Ber.*, **44**, 316 (1911).

[5] The Corpuscular Theory of Matter, 1907, Chap. IV.

[6] *Ber.*, **46**, 184 (1913), cf. Keesom, *Phys. Z.*, **14**, 670 (1913).

[7] *Phil. Mag.*, **29**, 127 (1915).

[8] *Ber.*, **52**, 506, 990 (1919); cf. Borelius, *Ann. Physik*, **57**, 278 (1918).

[9] The experiments of Franck and Hertz, *Verh. Deut. Phys. Ges.*, **15**, 929 (1913); *Phys. Z.*, **14**, 1115 (1913), render this assumption fairly plausible.

When a P.D. is applied, the electron space lattice [1] shifts as a whole through the atomic space lattice, the attraction of the more distant ions being counterbalanced by the repulsion of the inflowing electrons: "in other words," as Lindemann says, "the electron space lattice or crystal may be said to melt at one end and fresh layers may be said to freeze on at the other, when a current flows."

If a_0, the limit of the action of the repulsive force of the ions, is less than $\frac{1}{2}a$, where a is the distance between two atomic centers, the electron lattice may glide unimpeded through the atomic lattice, provided the atoms are at rest or their vibration does not exceed $\frac{1}{2}a - a_0$ in amplitude. The latter condition corresponds to the super-conductivity of Onnes in the region of the absolute zero. As the temperature increases the atomic amplitude increases and resistance is offered to the electron lattice.

Lindemann does not enter into any detailed calculation, but a dimensional relation leads to

$$r = 1/\kappa = p^{1/2}N^{-2/3}\lambda^{-1/2}E,$$

where p is the density of the electron lattice, and E is bA^2, A being the amplitude of the vibrating particle and b the quasi-elastic force holding the atoms in position. Similarly

$$\theta = N^{-1/3}p^{-1/2}\sigma^{-3/2},$$

σ being the compressibility and θ the thermal conductivity. Thus,

$$\theta/\kappa = N\lambda^{-1/2}\sigma^{-3/2}E = \text{const.} \times E,$$

which is the Wiedemann-Franz law, since E is proportional to A, or T. The second assumption made at the beginning is necessary to calculate the value of the constant. The absence of an electron term $(3/2)N_0kT$ in the energy of the metal is accounted for on Lindemann's theory. Other theories have been put forward by Herzfeld,[2] Hauer,[3] Gruneisen,[4] and others. Gruneisen finds that the specific resistance of pure metals is at low temperatures a universal function of $T/\beta\nu_m$, where β is the radiation constant $= h/k$, and ν_m the characteristic frequency. The ratio of resistivity to absolute temperature is proportional to the atomic heat of the metal. The variation of resistance with pressure confirms the view that the mean free path of the electrons is inversely proportional to the square of the amplitude of the vibrating atoms, which is in agreement with Lindemann's equations. Beckman [5] showed that in many cases the change of resistance with pressure is in agreement with Gruneisen's views.

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[1] Cf. Born and Kármán, *Phys. Z.*, **13**, 297 (1912); **14**, 15, 65 (1912); Born, *Ann. Physik*, **44**, 605 (1914); Dynamik der Kristallgitter, Berlin and Leipzig, 1915; Reiche, Quantum Theory, Eng. tr., 1922, p. 42.

[2] *Ann. Physik*, **41**, 27 (1913).

[3] *Ibid.*, **51**, 189 (1916).

[4] *Ber. Deut. phys. Ges.*, **15**, 186 (1913); **20**, 36 (1918).

[5] *Phys. Z.*, **16**, 59 (1915); **18**, 507 (1917): the result does not hold for Bi, Hg, Tl, Ta, Mo; if p is the pressure and δr the resistance change, then $\delta r = ap + bp^2$, where a and b are constants, holds for many metals, *e.g.*, Zn, Fe, Pd, etc.

Benedicks[1] and Grüneisen[2] have shown that atomic conductance is a periodic function of atomic weight and decreases in value from the first to the eighth group in the periodic table. Streintz[3] found that between 18° and 100° the relation

$$\sqrt[3]{\textit{atomic volume}} = \text{const.} \times dr/dT$$

holds for certain series of metals, such as Pd, Pt, Al, Ag, Au, Cd, Sn. The constant appears to vary from series to series, and to depend, to some extent, on the atomic volume of the metal.[4]

Effect of Temperature on Resistance of Metals: The relation between the specific resistance of a metal and temperature may be expressed by the formula:

$$r = a + bT + cT^2;$$

for small ranges of temperature the linear relation

$$r = a + bT$$

is sufficient, the coefficient having the value about $(1/r)dr/dT = 0.004$ (cf. coefficient of expansion of a gas), although for magnetic metals it is higher. The coefficient increases with temperature, large changes being observed in the neighborhood of transition points and melting points. The coefficients for liquid metals are usually 1.5 those for solid.[5] Unlike the corresponding constants for gases, $(1/r)(dr/dT)_p$ and $(1/r)(dr/dT)_v$ are different. In the case of mercury,[6] the value at constant volume is -0.9×10^{-4}, that at constant pressure $+8.9 \times 10^{-4}$.

Lindeck[7] finds that (*specific resistance at a given temperature*) × (*temperature coefficient of resistance at the same temperature*) is constant for metals. For copper the constant has the value 6.78×10^{-9} at 15°. The constants for aluminium and iron are 11.6×10^{-9} and 58.5×10^{-9}, at 15°, respectively. The relation holds even in presence of impurities (e.g., As in Cu).

At very low temperatures the resistance diminishes very rapidly with the temperature, and at 3° or 4° abs. the resistance may be zero, i.e., the metal is a perfect conductor. Our knowledge of the resistance of metals at very low temperature is due to the work of Kamerlingh Onnes and his co-workers at Leyden.[8] In the case of mercury, for example, at 13.9° abs. the resistance is

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[1] *Jahrb. Radioakt. Elektronik*, **13**, 351 (1916).

[2] *Ber. Deut. phys. Ges.*, 20, 53 (1918).

[3] *Ann. Physik*, **33**, 436 (1910).

[4] Further papers on the conductivity of metals: Koenigsberger and Weiss, *Ann. de Phys.*, **35**, 1 (1911); J. J. Thomson, *Nature*, **96**, 494 (1915), *Phil. Mag.*, **43**, 721 (1922), **44**, 657 (1922); Bramley, *Phil. Mag.*, **46**, 1053 (1923)

[5] Somerville, *Phys. Rev.*, **31**, 261 (1910), **33**, 77 (1911)

[6] Kraus, *Phys. Rev.*, **4**, 159 (1914), Somerville, *loc. cit.*

[7] *Ber. Deut. phys. Ges.*, **13**, 65 (1911).

[8] *Proc. K. Akad. Wetensch. Amsterdam*, **13**, 1274 (1911), **14**, 818 (1912); **15**, 1406 (1913); **16**, 113, 673 (1913); **17**, 508 (1914), see also Clay, *Jahrb. Radioakt. Elektronik*, **8**, 383 (1911); **12**, 259 (1915); Crommelin, *Phys. Z.*, **21**, 274, 300, 331 (1920); *Chem. Weekblad*, **16**, 640 (1919).

0.034 that of solid mercury at 273°. At 4.3° abs. it is 0.0013 times, and at 3° abs. less than 0.0001 times. Gold and lead behave similarly. Metals at these low temperatures are said to be in a "super-conducting" state. Some metals, such as platinum, copper, and metals which tend to form solid solutions, do not become super-conducting, but the resistance decreases to a minimum, and then rises again with further fall in temperature.

An apparatus for the measurement of resistance of metals at very high temperatures has been devised by Saldau.[1]

Conductivity of Alloys: The electrical conductivity of alloys[2] is characteristic. Each component contributes to it, so that if an alloy is purely a mechanical mixture its conductivity is an additive property of the volume percentages of the components. Isomorphous mixtures have a conductivity which is always less than that calculated from the mixture law, and is diminished by addition of foreign substances. The formation of a solid solution is accompanied by considerable increase in the resistance of the alloy, and this increases also with increase of concentration.[3] When the components form a compound this possesses a peculiar and characteristic conductivity which is relatively high, and is diminished by additions of foreign substances. The temperature coefficients of intermetallic compounds differ but little from the normal value (0.004) for pure metals.[4]

In the case of solid solutions the temperature coefficients are much lower.[5]

Lord Rayleigh[6] showed that the application of an E.M.F. to an alloy should call into play opposing thermoelectric forces, due to the Peltier effects at the numerous boundaries between the different metals, and, according to Liebenow,[7] this is the reason why the conductivity of alloys consisting of different kinds of molecules is always less than according to the mixture rule. From this assumption the properties of alloys can be deduced,[8] except those of solid solutions, when the explanation of Rayleigh seems to break down.[9]

[1] *Iron and Steel Inst. Carnegie Schol. Mem.*, **7**, 195 (1916).

[2] Desch, Metallography, London, 1922, 253; Guertler, *Jahrb. Radioakt. Elektronik*, **5**, 17 (1908); Le Chatelier, *Revue générale des sciences*, **6**, 531 (1895); Contribution à l'étude des alliages, Paris, 1901, 446, Skaupy, *Ber. Deut. phys. Ges.*, **18**, 252 (1916); Schenck, *Ann. Physik*, **32**, 261 (1910).

[3] Pushin and Maximenko, *J. Russ. Phys. Chem. Soc.*, **41**, 500 (1909); Chem. Abs., **5**, 819 (1911); Pushin and Dishler, *ibid.*, **44**, 125 (1912); Chem. Abs., **6**, 1587 (1912); N. I. Stepanoff, *ibid.*, **44**, 910 (1912); Chem. Abs., **6**, 2187 (1912); Kurnakoff and Schemtchuschny, *ibid.*, **39**, 211 (1907); Norbury, *Trans. Faraday Soc.*, **16**, 570 (1920).

[4] Pushin and Dishler, *loc. cit.* Alloys of brittle and easily oxidized metals can be suitably cast according to the method of N. J. Stepanoff, *Z. anorg. Chem.*, **60**, 209 (1908); *J. Russ. Phys. Chem. Soc.*, **40**, 1448 (1908); Chem. Abs., **3**, 773 (1909). On solid solutions see also Guertler, *Z. anorg. Chem.*, **51**, 397 (1906).

[5] N. I. Stepanoff, *loc. cit.*

[6] *Electrician*, **37**, 277 (1896); *Nature*, **54**, 154 (1896); *Collected Papers*, iv, 232; experimental demonstration, Pushin and Maximenko, *loc. cit.*, Willows, *Phil. Mag.*, **12**, 604 (1906).

[7] *Z. Elektrochem.*, **4**, 201 (1897); Der elektrische Widerstand der Metalle, Halle, 1908.

[8] Nernst, Theoret. Chem., 8–10 Aufl., p. 471.

[9] Desch, Metallography, 1922, 255; Schenck, *Metallurgie*, **4**, 161 (1907); *Physik. Z.*, **8**, 239 (1907); Guertler, *Z. anorg. Chem.*, **54**, 58 (1907).

Matthiessen[1] put forward the general law that the conductivity of a binary alloy may be represented by the equation

$$\kappa_m/\kappa = P_m/P,$$

where κ and κ_m are the observed conductivity and that calculated from the mixture rule, respectively, and P and P_m are the corresponding temperature coefficients. Since $P_m = 100(\kappa_0 - \kappa_{100})/\kappa_0$ for all metals is equal to 29 ± 2, we can write the law $\kappa_m P/\kappa = 29 \pm 2$. For alloys free from mixed crystals, $\kappa_m = \kappa$, and the rule becomes $P = 29 \pm 2$.

The correctness of Matthiessen's law has been demonstrated by other experimenters.[2] The law has been modified by Guertler,[3] who states that the conductivity of a binary alloy and its temperature coefficient are proportional, even when mixed crystals and compounds are present. In all cases the conductivity and temperature coefficient curves have the same form. Guertler and Schulze[4] state the law in the form that the absolute increase in resistance on raising the temperature of a binary alloy from 0° to 100° is independent of the increase of resistance brought about by the presence of mixed crystals and has the same value as that calculated from the increase of resistance of the pure components when raised through the same temperature interval. That is, $dr_m/dt = dr/dt$. This is confirmed by experiment

The constitution of binary alloys may be deduced from conductivity measurements.[5] The following are the most important results: (1) Alloys for which the electrical conductivity is a linear function of the volume composition have components not miscible in the solid state. (2) Alloys forming a complete series of solid solutions (e g., Ag Au) have a continuous conductivity curve (plotted against volume concentration). This curve shows a very flat minimum and falls rapidly on both sides from the points representing the conductivities of the pure metals. (3) The components of some alloys exhibit only limited miscibility: in this case the last statement holds for that part of the curve between the pure metals and the saturated solid solutions, while the first statement holds for that part of the curve between the compositions of the saturated solid solutions. (4) If two metals form m compounds, the conductivity-concentration diagram can be divided into $m + 1$ single binary diagrams, and from the shape of the curves information on the existence of compounds may be obtained. (5) The electrical conductivity of a system can never exceed the values on the straight line joining the conductivities of the pure components. (6) A sharp point on the curve always indicates the presence of a chemical compound, but the converse does not hold, although Liebenow considers that it does.

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[1] *Ann. Physik*, **112**, 353 (1861).

[2] Matthiessen and Vogt, *Ann. Physik*, **122**, 19 (1864); Dewar and Fleming, *Phil. Mag.*, **34**, 326 (1892); **36**, 271 (1893); Reichardt, *Ann. Physik*, **6**, 832 (1901), etc. References in Guertler, *Z. anorg. Chem.*, **54**, 72 (1907), *Z. Elektrochem.*, **18**, 601 (1912).

[3] *Loc. cit.*

[4] *Z. physik. Chem.*, **104**, 90 (1923)

[5] Guertler, *Z. anorg. Chem.*, **51**, 397 (1906); *Z. Elektrochem.*, **18**, 601 (1912); *J. Inst. Metals*, **6**, 135 (1911).

The constitution of alloys may also be elucidated from a consideration of the temperature coefficients of conductivity.[1] The value of P, the percentage decrease in conductivity on raising the temperature from 0° to 100°, is the same for alloys free from mixed crystals (solid solutions) and for pure metals, so that alloys for which $P = 31$ or more contain no solid solutions (magnetic alloys excepted). Alloys containing solid solutions have a value of P which falls rapidly from the value for pure metals, and the curves connecting P with the composition of the alloys show in many cases breaks corresponding with those in the miscibility of the metals. The resistance of solid solutions is supposed to persist even at the absolute zero, whereas that of pure metals tends to vanish at $T = 0$. The values of the Wiedemann-Franz constant θ/κ are smaller when solid solutions are formed than with pure metals.[2] When solid solutions are not formed, it has the same value as for pure metals.

Conductivity of Liquid Alloys and Amalgams: Very little work has appeared on the conductivities of liquid alloys. Some experiments have been made by Bornemann and Müller,[3] glass or quartz vessels being used. Liquid alloys of sodium and potassium give a curve typical of a continuous series of solid solutions (Ag–Au), with a well-marked minimum. There is no indication of the compound Na_2K, but NaK appears to exist. Liquid alloys of lead and tin exhibit a conductivity which varies linearly with composition. The curve for liquid alloys of copper and nickel is continuous with a distinct minimum; that for copper and antimony shows a break at Cu_3Sb,[4] which is more strongly marked in the curve of temperature coefficients. The influence of added metal on the conductivity of a liquid metal is quite independent of the conductivity of the added metal. The determining factor seems to be tendency to compound formation. The alkali metals, having a strong tendency to combination, always lower the conductivity of a liquid metal to which they are added, whilst indifferent metals may either raise or lower it.

The conductivity of mercury is lowered by addition of alkali metal, but raised by addition of other metals.[5] The low temperature coefficient of mercury [6] has been attributed to the presence of two or more different kinds of molecules giving it the properties of an alloy. The addition of alkali metals (except lithium) which form compounds with mercury, and increase the number of complex molecules, lowers its conductivity in accordance with this view, whilst indifferent metals (lithium, calcium, strontium), which dissolve in the monatomic form, raise it.[7] The effect increases with temperature. The conductivity curve for amalgams exhibits a maximum corresponding with

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[1] Guertler, *Z. anorg. Chem.*, **54**, 58 (1907).

[2] Schulze, *Ann. Physik*, **9**, 555 (1902).

[3] *Metallurgie*, **7**, 396 (1910), Bornemann and Wagenmann, *Ferrum*, **11**, 276, 289, 330, (1914); Müller, *Metallurgie*, **7**, 730, 755 (1910).

[4] Bornemann and Rauschenplat, Metallurgie, **9**, 473, 505 (1912).

[5] Bornemann and Müller, Metallurgie, **7**, 396 (1910).

[6] About 0.001; Liebenow, Die elektrische Widerstand der Metalle.

[7] Fenninger, Diss., Freiburg, 1914, Lewis, Adams and Lamman, *J. Am. Chem. Soc.*, **37**, 2656 (1915), attribute the lowering in conductivity to a reduction in the average mobility of the electrons.

$NaHg_2$[1] and one corresponding with KHg. Metals dissolved in mercury are assumed by Skaupy[2] to be ionized to a considerable extent. Lewis, Adams, and Lamman[3] found transfer of alkali metal from kathode to anode in the electrolysis of sodium amalgams, and assumed that the sodium atoms form nuclei on which large aggregates of mercury atoms collect, the whole aggregate being less easily penetrated by electrons than free mercury atoms.

The Conductivity of Solid Salts and Glass: Some experiments on the conductivities of solid sulphides were made by Faraday.[4] In the case of silver and lead halides, no sudden change of conductivity occurs on fusion.[5] In other cases sudden changes occur on fusion,[6] or when the substance passes through a transition point.

Experiments on the conductivity of glass[7] show that the sodium ions move.

The conductivities of mixed oxides were investigated by Reynolds,[8] who used principally zirconium and cobalt oxides, with various added oxides. With increasing concentration of the latter the conductivity passes through a maximum. The true electrolytic character of the conduction in such mixtures was established by Nernst[9] and Bose.[10] The Nernst lamp[11] makes use of these results. Graetz[12] found that the conductivity of solid salts is increased by compression. Arrhenius[13] found the conductivities of silver chloride and bromide to be affected by light. Brown[14] found the conductivity of solid copper ferrocyanide to take place without polarization. A very complete investigation of the conductivities of solid salts was made by J. Rosenthal.[1] He cast or pressed the substance into sticks, bored holes in these, covered the insides with graphite, and inserted platinum wires which were fixed in place with Rose's metal. The results, although numerous, were more or less qualitative. In some cases the crystalline form conducted better than the amorphous, sometimes both equally well. The conductivity of lead chloride changed with time, probably owing to change of modification. Some salts conducted only at higher temperatures (e.g., $K_2Cr_2O_7$ above 310°). Foussereau[2] measured the conductivities at various temperatures, and found that the specific resistances could be represented by equations of the form:

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[1] Cf. Hine, *J. Am. Chem. Soc*, **39**, 879 (1917), who finds that the conductance of sodium amalgam passes through a minimum Cf Vanstone, *Trans Farad Soc* **9**, 291 (1914)

[2] *Ber. Deut physikal Ges*, **18**, 252 (1916).

[3] *J. Am. Chem. Soc*, **37**, 2656 (1915)

[4] *Phil. Trans.*, **123**, 507 (1833), Expt Res, 4th Series, 410 ff, 7th Series, 201.

[5] E. Wiedemann, *Ann. Physik*, **154**, 318 (1875), W Kohlrausch, *ibid*, **17**, 642 (1882), Ayrton, *Phil. Mag*, **6**, 132 (1878), L Poincaré, *Ann Chim Phys*, **21**, 289 (1890), Graetz, *Ann Physik*, **40**, 18 (1890), Lapschin and Tichanowitsch *Bull Acad Petersb*, vol 4 (1861), Tubandt, *Nernst Festschrift*, p. 446 (1912), Tubandt and Lorenz, *Z physik Chem*, **89**, 513 (1914).

[6] T. Andrews, *Proc Roy Soc Edin*, **13**, 275 (1884), W Kohlrausch, *Ann Physik*, **17**, 642 (1882) (AgI), S. P Thompson, *Nature*, **24**, 469 (1881) ($HgCu_2I_4$), Beetz, *Ann. Physik*, **92**, 452 (1854), *ibid*, *Jubelband*, 23 (1874) (HgI_2) Lorenz, *Elektrolyse geschmol Salze*, ii, 241 ff., Gros, *Sitz. ber Preuss. Akad*, 500 (1877)

[7] Warburg, *Ann. Physik*, **21**, 622 (1884), T Gray, A Gray, and Dobbie, *Proc. Roy Soc*, **36**, 488 (1884); F. Tegetmeier, *Ann Physik*, **41**, 18 (1890), Kraus and Darby, *J Am Chem. Soc*, **44**, 2783 (1922), LeBlanc and Kerschbaum, *Z physik Chem*, **72**, 468 (1910), Speranski, *J Russ. Phys. Chem Soc*, **47**, 52 (1915), Pirani and Lax, *Z techn Physik*, **3**, 232 (1922), Pirani and Siemens, *Z. Elektrochem*, **15**, 969 (1909), Haber, Thermodynamics, Eng tr 1908, 318, Winkelmann's Physik, IV, i, 452, Lorenz, Elektrolyse geschm Salze, ii, 229ff

[8] *Diss.*, Gottingen, 1902

[9] *Z. Elektrochem.*, **6**, 41 (1899).

[10] *Ann. Physik*, **9**, 164 (1902).

[11] *Elektrotechn Z*, **19**, 272 (1898), **22**, 400, 620 (1901), **24**, 281, 442 (1903), **25**, 610, 751 (1904). Zirconia and thoria, with rare earths, are used. See also Zimmerman, *Trans Am Electrochem. Soc*, **7**, 79 (1905), who finds electrolysis takes place in Nernst filaments.

[12] *Ann. Physik*, **29**, 314 (1886).

[13] *Wien. Akad. Ber.* **96**, 831 (1887), *Beibl Ann Physik*, **12**, 119 (1888).

[14] *Phil. Mag*, **33**, 82 (1891).

$$\log r = a - bt + ct^2,$$

where t = temperature. The conduction is attended by movement of ions, although this is extremely slow.[3]

The following method is described for the measurement.[4] The powder is strongly compressed[5] into small cylinders, the ends of which are covered with a thin layer of graphite. Connection is made with the circuit by means of platinum plates pressed firmly against the ends.[6] Kohlrausch's method is used for the measurement. In the case of potassium, sodium and silver nitrates the resistance of the crystalline substance is more than 10,000 times that of the fused, and the relation

$$\log \kappa = a + bt \quad (t = \text{temperature, } a \text{ and } b \text{ constants})$$

holds. The conductivity of solid solutions always exceeds that of the components, the reverse being the case for metals. Similar results were found for silver, potassium and sodium chlorides, and potassium chromate,[7] but in the binary system AgCl-KCl the conductivity is the sum of those of the constituents, since these are not miscible. The sudden changes at melting or transition temperatures are proposed in the measurement of these temperatures.[8] The conductivity isotherms used for alloys do not represent the results with solid mixtures of salts.[9]

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[1] *Ann. Physik*, **43**, 700 (1891).

[2] *Ann. Chim. Phys.*, **5**, 241, 317 (1885).

[3] von Hevesy, *Z. Physik.*, **2**, 148 (1920).

[4] Benrath, *Z. physik. Chem.*, **64**, 693 (1908).

[5] Ketzer, *Z. Elektrochem.*, **26**, 77 (1920), finds that the conductivity may change as much as 12 per cent according to the pressure used in making the cylinders.

[6] Tubandt, *Z. anorg. Chem.*, **115**, 103 (1921), finds that the interposition of a cylinder of cubic silver iodide between the kathode and cylinder of salt is an improvement when direct current is used. It prevents possible short circuiting owing to the formation of a metal bridge, which is one of the chief difficulties; cf. Tubandt and Eggert, *ibid.*, **110**, 196 (1920).

[7] Benrath and Wainoff, *Z. physik. Chem.*, **77**, 257 (1911). On the conductivity of crystals see Doelter, *Monatsh.*, **31**, 498 (1910).

[8] Benrath, *Z. physik. Chem.*, **64**, 693 (1908); cf. Tubandt and Lorenz, *ibid.*, **87**, 513 (1914).

[9] Benrath and Tesche, *Z. physik. Chem.*, **96**, 474 (1920).

Haber and Zawadzki[1] found that when solid compressed silver salts (halides, sulphate) are electrolyzed between silver plates, polarization occurs, which is greater the lower the temperature and increases when the salts are kept compressed for some time. They suggest that the current is transported by electrons, with simultaneous formation of oxidizing materials such as free halogens or silver persulphate, which then attack the anode.

The conductivities of some powders were investigated by Goddard, who found that in the case of silver iodide[2] the conductivity fell rapidly at first, then reached a limiting value, rising, at first rapidly and then slowly, to its initial value when the circuit was broken. The conductivity of barium sulphide was constant for the solid, but rose when the substance was powdered. The conductivity of powdered molybdenite rose on the application of E.M.F. Ohm's law is not obeyed for powders except in the case of zinc perborate. The conductivity of a powder falls in a vacuum, at first rapidly, then slowly.

The conductivity of solid calcium sulphide increases rapidly with the temperature and also under the influence of light up to a point,[3] the curve showing an acute maximum, from which it descends to zero as the temperature is raised still higher. The phenomenon is probably connected with the state of phosphorescence.

Sandonnini[4] found that the conductivity isotherms of the system $PbCl_2$-$PbBr_2$ at 200°, 250° and 300° all show a minimum corresponding approximately to equimolecular proportions. In the system AgCl-AgBr, examined at 200°, 250°, 300°, 350° and 400°, the conductivities of mixtures containing between 0 and 70 molar per cent of bromide are less, and those of the remaining mixtures slightly greater than the values calculated by the law of mixtures. The conductivities of solidified mixtures of salts are less than those calculated additively when they form perfectly homogeneous solid solutions with melting points intermediate between those of their components. When the components form mechanical mixtures and no other phenomenon interferes, the conductivities should be strictly additive. Benrath (above) found that this additive value is always exceeded, the only apparent cause for which lies in the gradual diminution of internal friction because the maximum is observed at a point where the conductivity isotherm lies close to the eutectic point. The large increases in conductivity found by Fritsch[5] on mixing halides of lead and mercury with those of alkali metals, when solid solutions were supposed to be formed, do not occur in the complete absence of moisture and if the mixture is not overheated. LeBlanc,[1] who measured the conductivities at 18° of lead, potassium and barium fluorides and mixtures of these, found that the conductivity of lead fluoride is doubled by the addition of 5 per cent of barium fluoride, and becomes five times as great by the addition of 5 per cent of potassium fluoride. The increases are smaller than those found by Fritsch.

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[1] *Z. physik. Chem.*, **78**, 228 (1912).

[2] *Phys. Rev.*, **28**, 405 (1909).

[3] Vaillant, *Compt. rend.*, **154**, 867 (1912), **171**, 1380 (1920), cf Pélabon, *ibid.*, **173**, 142, 295 (1921) (thallous sulphide and selenide), **152**, 1302 (1911) (antimony selenides); on the unipolar conduction of stibnite see Martin, *Phys. Z.*, **12**, 41 (1911). The conductivity of finely divided salts is a function of the size of the particles, Fink, *J. Phys. Chem.*, **21**, 32 (1917).

[4] *Atti R. Accad. Lincei*, (v), **24**, i, 842 (1915), *Gazzetta*, **50**, i, 289 (1920). Ketzer, *Z. Elektrochem.*, **26**, 77 (1920), finds that the conductivity of solid lead chloride is largely influenced by previous treatment, and LeBlanc, *ibid.*, **18**, 549 (1912), finds the same with lead fluoride, potassium fluoride and barium fluoride.

[5] *Ann. Physik.*, **60**, 300 (1897).

Sometimes positive and negative ions are the carriers in solid salts. Tubandt[2] finds that with solid silver iodide, bromide, and chloride the current is carried entirely by the silver ion. Faraday's law holds to within 1 per cent with these salts and silver nitrate.[3] A layer of silver iodide was interposed between the salt and kathode. In the case of silver iodide the velocity of the silver ion in the solid was 0.55×10^{-3} cm./sec. per volt per cm. at 145° C., approximately the same as its value in aqueous solution at 18°, and double this value at 552°. In the case of lead chloride the current is carried by the chloride ion, and in lead fluoride by the fluoride ion. Above 180° silver sulphide is a true electrolytic conductor, the silver ion carrying the current and moving with a velocity of 0.11 cm./sec.[4] The cubic form of cuprous sulphide is a pure electrolytic conductor, the metal ions carrying the current.

Conductivity measurements with hydrogen absorbed in palladium have led to the conclusion that solid solutions,[5] or a solution of hydrogen, probably monatomic,[6] are formed.

Electrolysis of Fused Salts: After the experiments of Faraday, already mentioned, the problem of the conduction of fused salts was taken up by Matteucci[7] and by Braun,[8] both of whom paid careful attention to polarization, since direct current was used. Braun was led to a speculation as to the state of salts in solution which approaches the ionic theory.[9] The application of alternating current was made by Kohlrausch.[10] Foussereau[11] determined the specific conductivities of a number of fused salts by various methods, paying careful attention to polarization, the effect of temperature, and viscosity. Bouty and Poincaré[12] used the method which had been applied by Bouty to solutions (see later) and observed the conduction on the walls of the glass cell at high temperatures. They found that the conductivity of mixtures of similar salts was additive. Poincaré[1] then carried out an extensive investigation on the conductivities of fused salts at various temperatures. The conductivity increases with temperature more rapidly than linear proportionality, and the formula

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[1] *Z. Elektrochem.*, **18**, 549 (1912); see description of apparatus.

[2] *Z. anorg. Chem.*, **115**, 105 (1921).

[3] Cf. Tubandt and Eggert, *Z. anorg. Chem.*, **110**, 196 (1920).

[4] The α-form of Ag_2S follows Faraday's law exactly, Tubandt, Eggert and Schibbe, *Z. anorg. Chem.*, **117**, 1 (1921). Mixtures of Ag_2S and Ag do not follow the law (Tubandt and Eggert, *ibid.*, **117**, 48) until all the free silver has migrated to the kathode and pure Ag_2S remains.

[5] Sieverts, *Internat. Z. Metallographie*, **3**, 36 (1912).

[6] Smith, *Proc. Nat. Acad. Sci.*, **7**, 28 (1921).

[7] *Ann. de Chim.*, **15**, 498 (1845).

[8] *Ann. Physik*, **154**, 161 (1875).

[9] Lorenz, Elektrolyse geschm. Salze, ii, 194.

[10] *Ann. Physik*, **17**, 642 (1882).

[11] *Ann. Chim. Phys.*, **5**, 241, 317 (1885).

[12] *Ann. Chim. Phys.*, **17**, 52 (1889).

$$\kappa_t = \kappa_0[1 - a(t - t_0)]$$

was not exactly obeyed. The product ad, where d = density, was constant. The ratio of the molecular conductivities of sodium and potassium salts was independent of the anion. An extensive series of measurements was also made by Graetz.[2] The subject has, however, been principally advanced by the work of Richard Lorenz and his co-workers.[3]

The principal difference from the case of solutions is that, whereas in the latter case mixtures of solute and practically non-conducting solvent are involved, in the case of fused salts either only one substance is present or the components are conductors of the same class. In spite of this great difference the ions deposited are the same in both cases, and Faraday's law is obeyed, with the same value of F = 96,500 coulombs (see "Faraday's Laws"). In the deposition of silver the accuracy is 0.005 per cent up to 260°, and 0.9 per cent up to 640°; with lead the accuracy is about 1 per cent up to 1050°.[4]

The conductivity is mainly conditioned by the temperature, and the attempt to connect it with the degree of ionization, as in the case of solutions (*q. v.*), is not possible.[5] Polarization is observed in the electrolysis of fused salts, and cells of the Daniell type, as well as those with liquid junctions, may be set up with fused salts,[6] the E.M.F.'s being of the same order as in aqueous solutions. Freezing point measurements indicate that complex salts are sometimes formed, and complex ions are therefore probably present. Surface tension measurements indicate strong association[7] of fused salts.

The migration of ions has been observed in the case of fused salts,[8] but migration ratios cannot be calculated, since "solvent" is identical with "solute." In the case of a particular mixture of lead chloride and potassium chloride containing about 7 per cent of the former, all the lead deposited is taken from the vicinity of the kathode and no lead ions move through the mass of the liquid.

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[1] *Ann. Chim. Phys.*, **21**, 289 (1890); *Compt. rend.*, **108**, 138 (1889); **110**, 339 (1889).

[2] *Ann. Physik*, **40**, 18 (1890).

[3] Elektrolyse geschmolzener Salze, 3 parts, Halle, 1905–6; *Z. physik. Chem.*, **70**, 230 (1910); the following account is mainly derived from these sources, except for later work.

[4] Cf. Bruni and Scarpa, *Atti R. Accad. Lincei*, **22**, i, 138 (1913); Tubandt and Lorenz, *Z. physik. Chem.*, **87**, 513 (1914).

[5] Lorenz, *Z. physik. Chem.*, **70**, 330 (1910).

[6] Lorenz, *loc. cit.* No polarization was observed in the electrolysis of potassium iodide in fused iodine, G. N. Lewis and Wheeler, *Z. physik. Chem.*, **56**, 179 (1906). Cf. Lorenz, Elektrolyse, iii, 1 ff. for details.

[7] Lorenz, *Z. physik. Chem.*, **70**, 238 (1910); Walden, *Bull. Acad. Petersb.*, 405 (1914); *Z. physik. Chem.*, **75**, 555 (1910); Walden and Swinne, *ibid.*, **79**, 700 (1912); **82**, 271 (1913); Liebmann, *Diss.*, Zurich, 1909; Hochberg, *Diss.* Frankfort a. M., 1915; Lorenz and Hochberg, *Z. anorg. Chem.*, **94**, 301 (1916).

[8] Lorenz, *Z. physik. Chem.*, **70**, 234 ff. (1910).

The experimental methods of determining the conductivities of fused salts have been described by Lorenz (loc. cit.).[1]

Lorenz and Schultze investigated the conductivity of fused zinc chloride between 250° and 700° in a hard glass cell with silver electrodes, resembling the Arrhenius cell. Lorenz and Kalmus used platinum electrodes in a hard glass or quartz cell, two circular electrodes being separated by a capillary vessel. Aten used carbon electrodes; for good conductors a peculiar type of cell was used.[2] A general source of error is the conduction of the glass at high temperatures. Arndt used porcelain U-tubes with platinum electrodes. Arndt and Gessler[3] worked up to 1100°.

The chief sources of error in the measurements are:[4] (1) evaporation of deposited metal, increasing at higher temperatures; (2) chemical side reactions (e.g., $Ca + CaCl_2 = 2CaCl$); (3) cloud formation, when the metal does not separate in compact form but is diffused through the fused electrolyte in the form of a very fine cloud or mist;[5] (4) colloidal solution of metal in the electrolyte; (5) complex formation at the anode; (6) recombination of the deposited substances. The formation of fog may be prevented to some extent by the addition of another salt, e.g., KCl to $PbCl_2$, $BaCl_2$ to $PbCl_2$, etc., the effect being supposed to depend on changes of surface tension between the metal and fused salt.[6]

The conduction of fused salts is characterized by Lorenz as of the Grotthus type (see later), as contrasted with the Hittorf type (moving ions) in the case of solutions.[7] From considerations of the ionic radius he supposes that there is an exchange between ions and molecules.[8] An approximate calculation gave the dissociation of $NaNO_3$ as 31.5 per cent at 388°. The method of calculation is as follows. The Hittorf conductivity is obtained by dividing the observed conductivity by 2, since the speed of the ions is 2 to 3 times that calculated from the atomic radii, and the limiting value is found by Einstein's formula, making use of the viscosities and radii of the ions in water and in the fused salt.[1] It is assumed that the effect of temperature on the degree of ionization may be neglected.[2] Einstein's formula gives for the velocity of motion of a particle of radius r in a medium of viscosity η the value:

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[1] Cf. Lorenz and Kalmus, *Z. physik. Chem.*, **59**, 17 (1907), Schultze, *Z. anorg. Chem.*, **20**, 323, 333 (1899); Helfenstein, *ibid.*, **23**, 255 (1900), Lorenz, *ibid.*, **23**, 97 (1900); Grünauer. *ibid.*, **39**, 389, 404 (1904) (very detailed); Quincke, *Ann. Physik*, **36**, 270 (1889); Aten, *Z. physik. Chem.*, **73**, 578 (1910); **78**, 1 (1912); Arndt, Physikalisch-Chemische Technik. p. 592; *Ber.*, **40**, 2937 (1907), cf. Lorenz, *ibid.*, 3308, 4378, Jaeger and Kapma, *Z. anorg. Chem.*, **113**, 27 (1920); Appelberg, *ibid.*, **36**, 36 (1903); Auerbach, *ibid.*, **28**, 1 (1901), Lorenz. Elektrolyse, i and ii. According to Faraday, Expt. Res., 5th Series, 1833, p. 133, Davy in 1802 found that fused nitre, caustic potash and soda are conducting. Faraday (*loc. cit.*) investigated many fused salts and found that they were decomposed according to the law of electrochemical equivalents. The great influence of traces of moisture on conductivity was realized by Schultze, *Z. anorg. Chem* , **20**, 323, 333 (1899).

[2] *Z. physik. Chem.*, **66**, 653 (1909).

[3] *Z. Elektrochem.*, **14**, 662 (1908). Cf. Goodwin and Mailey, *Phys. Rev.*, **26**, 28 (1908).

[4] Lorenz, Elektrolyse, ii, 32 f.

[5] This is shown especially in the electrolysis of lead salts in electrolytes containing alkalies, it increases with temperature. See Lorenz and Helfenstein, *Z. anorg. Chem.*, **23**, 255 (1900), Schultze, *ibid.*, **20**, 323 (1899), Grünauer, *ibid.*, **39**, 389 (1904), Lorenz, Elektrolyse, i, 136 f., ii, 40 f.

[6] Lorenz, *Z. Elektrochem.*, **13**, 582 (1907), *Nernst Festschrift*, 266 (1912); Lorenz and Appelberg, *Z. anorg. Chem.*, **36**, 36 (1903); Walden, *loc. cit.*

[7] *Z. physik. Chem.*, **79**, 63 (1912); Fleck and Wallace, *Trans. Farad. Soc.*, **16**, 346 (1920), think that, since Ohm's law is strictly obeyed by fused caustic soda, the ions are already formed and no energy is required to disrupt the molecule. The argument is not decisive against Lorenz's theory, since the energy of recombination has not been taken into account.

[8] *Z. physik. Chem.*, **73**, 253 (1910).

$$u = K/6\pi\eta r N_0,$$

where N_0 = number of molecules per gram molecule and K is the driving force applied to the particle. If K is in dynes, u is given in cm. per sec., and the constant is then calculable. It is assumed that the mobilities in water and in the fused salt are inversely proportional to the viscosities and radii (as indicated by the formula):

$$u_u/u_s = \eta_s r_s/\eta_u r_u,$$

and further that the radius of the ion is, at least very approximately, the same in both cases, i.e., $r_s = r_u$. The value of the limiting equivalent conductivity (see later) is then given by

$$\Lambda_\infty = (u_u + v_u)\frac{\eta_u}{\eta_s},$$

also $\Lambda = \kappa/c$, where c is the concentration of the fused salt It will be seen that the calculation is somewhat speculative in character.

The measurement of the viscosities of fused salts is described by Lorenz.[3]

The experiments of Poincaré (*loc. cit.*) indicate that the ionization of a fused binary salt is independent of temperature, the changes of conductivity being determined by changes of viscosity When a fused salt solidifies, an enormous change of conductivity occurs, but Sachanow[4] considers that this is entirely accounted for by the great viscosity change, and that salts are ionized to the same extent in the solid and liquid states. This is in harmony with the most recent views on the structure of crystals (see later).

The conductivities of salts dissolved in fused salts have been measured by various investigators. The molecular conductivities of such solutions are high and usually decrease with dilution, whilst the opposite holds for aqueous solutions.[1] Measurements with chlorides of cæsium, potassium, sodium, ammonium, copper (cuprous) in fused mercuric chloride at 282° with platinum electrodes in a special apparatus were made. Solutions of mercurous chloride in the same solvent were non-conductors. Chlorides of bivalent metals are nearly all insoluble in fused mercuric chloride. Sackur[2] found that the laws of dilute solutions held for solutions of silver and cuprous chlorides in fused sodium and potassium chlorides for concentrations up to normal. By E.M.F. measurements he found that the ionization of the solutes is of the order of 10 per cent, and is independent of concentration.

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[1] *Z. physik. Chem*, **73**, 252 (1910)

[2] *Z. physik. Chem.*, **79**, 63 (1912), *Ber.*, **40**, 3308 (1907), table of values of Λ_∞ in *Z. physik. Chem.*, **79**, 65 (1910).

[3] *Z. physik. Chem.*, **73**, 244 (1910), Lorenz and Appelberg, *Z. anorg Chem*, **36**, 36 (1903), Tubandt and Lorenz, *Z. physik. Chem*, **87**, 513 (1914), Arndt, Physikal. Chem. Technik, 1915, p. 585, Walden, *Bull. Acad. Sci Petersb*, 405 (1914). Schulze, *Z. Elektrochem.*, **19**, 122 (1913), finds the degree of ionization of fused AgCl to be 1.17×10^{-3} to 1.35×10^{-3} at 461°, and of AgBr, 2.35×10^{-4} at 450°, in agreement with Abegg's values, based on E.M.F. measurements (*ibid.*, **5**, 353 (1899)). Electrolysis of fused ICl and IBr, Bruner and Bekier, *Z. Elektrochem*, **18**, 368 (1912).

[4] *J. Russ. Phys. Chem. Soc.*, **48**, 341 (1916). Lorenz, Elektrolyse, III, 289.

Electrolysis of solutions of lithium carbide in molten lithium hydride leads to separation of carbon at the anode, whence it is concluded[3] that the carbide is ionized. Nitrides of alkaline earth metals in the corresponding hydrides as fused solvents appear to be similarly ionized. Lithium hydride itself, in the fused state, gives hydrogen at the anode[4] and probably ionizes as $Li^+ + H^-$.

The conductivities of mixtures of fused salts[5] are less than those calculated by the mixture law, and the isotherms sometimes exhibit minima, indicating combination. No singular points are shown when combination occurs, except in the case $KCl-CaCl_2$. Benrath and Drekopf[6] measured the specific conductivity of molten mixtures of K_2SO_4 with Na_2SO_4, $MgSO_4$, KF, and Li_2SO_4. They find that the eutectic is a well-defined conductivity point. The specific conductivity depended on temperature according to the equation $\log \kappa + bT = \text{const.}$, which they also found to hold in the case of pure fused salts.

The electrical conductivity of fused salts is more complex than that of solutions, both from theoretical and experimental points of view.

✓ **Theories of Electrolysis:** *Grotthus' Theory:* An explanation of the fact that the products of electrolysis separated only at the poles was given by Grotthus in 1805.[7] He supposed that the passage of the current and the chemical effects were due to a series of successive decompositions and recombinations of the particles of the dissolved substance. In Fig. 1*a* let *AB*, *AB*, ⋯ represent molecules before the current passes; these are orientated by the attraction of the poles in the manner shown. The molecule next the positive pole is decomposed, the *B* ~~atom~~ ion being attracted and set free. The *A* atom ion, now without a partner, takes the *B* atom ion from the next molecule, and this goes on until at the end of the chain the unpaired *A* ~~atom~~ ion is set free. This stage is shown in Fig. 1*b*. All the molecules rotate so as to present *B* sides to the positive pole again, as in Fig. 1*c*, and the process is repeated. The cause of decomposition is thus assumed to be the attraction of the poles, which had been assumed by Berzelius and Hisinger[8] to vary inversely as some power of the distance from the pole. This view was disproved by Faraday.[1] He connected two platinum strips, kept at a fixed distance apart, with a galvanometer and immersed them in dilute acid through which a current was flowing. The deflection of the galvanometer was the same for all positions of the strips between the poles, indicating a constant force. Faraday also showed[2] that chemical decomposition could be produced without metal electrodes, e.g., by allowing the electric discharge from a pointed wire connected with a frictional machine to impinge on turmeric paper moistened with sodium sulphate solution, the other end being earthed. Alkali was liberated. He also showed[3] that when a current was passed through a strong solution of magnesium sulphate covered with a layer of water, magnesium hydroxide separated at the junction of the two liquids, although no electrode was situated there. From this and other experiments Faraday assumed that the decomposition was passed on from one salt particle to the next through the solution, and did not proceed where there were no contiguous salt particles, and he adopted a modification of Grotthus' theory[4] "the effect is produced by an internal corpuscular action exerted according to the direction of the electric current, due to a force either superadded to, or giving direction to the ordinary chemical affinity of the bodies present. The body under decomposition may be considered as a mass of acting particles, all those which are included in the course of the electric current contributing to the final effect; and it is because the ordinary chemical affinity is relieved, weakened, or partly neutralized by the influence of the electric current in one direction parallel to the course of the latter, and strengthened, or added to in the opposite direction, that the combining particles have a tendency to pass in opposite courses. . . . Particles *aa* could not be transferred or travel from the pole *N* towards the other *P* unless they found particles of the opposite kind *bb* ready to pass in the contrary direction." Also[5] "the free substance *cannot* travel, the combined one *can*."

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[1] Foote and Martin, *Amer. Chem. J.*, **41**, 451 (1909).

[2] *Z. physik. Chem.*, **83**, 297 (1913).

[3] Guntz and Benoit, *Compt. rend.*, **176**, 970 (1923).

[4] Moers, *Z. anorg. Chem.*, **113**, 179 (1920).

[5] Sandonnini, *Atti R. Accad. Lincei*, **24**, i, 616 (1915), *Gazetta*, **50**, i, 289 (1920).

[6] *Z. phys. Chem.*, **99**, 57 (1921).

[7] *Ann. Chim.*, **58**, 54 (1806); **63**, 20 (1808). The first paper was printed in Rome, 1805.

[8] *Ann. Chim.*, **51**, 167 (1804).

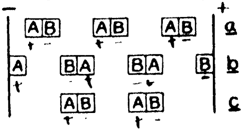

Fig. 1 Diagram illustrating Grotthus' Theory

Nomenclature: Faraday found it necessary to invent new names in the description of his experiments. The poles are only the doors or ways by which the electric current passes into or out of the decomposing body, hence they were called *electrodes* (ἤλεκτρον, amber, with which electrical effects are said first to have been observed, and ὁδὸς a way). The electrode by which the [positive] current entered was called the *anode* (ἄνω, upwards), that by which it left, the *kathode* (κατά, downwards). The material decomposed was called the *electrolyte* (ἤλεκτρον, and λύω, I loose). The bodies which move to the electrodes were called *ions*, that moving to the anode being the *anion*

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[1] Expt. Res., 1833, 5th Series, 144.

[2] Expt. Res., 1833, 5th Series, 131.

[3] Expt. Res , 1833, 5th Series, 140.

[4] Expt. Res., 1833, 5th Series, 149.

[5] Expt. Res., 5th Series, 157, the same theory is maintained by H. E. Armstrong, *Brit. Ass. Rep.*, p. 945 (1885); *Proc. Roy Soc.*, **40**, 268 (1886).

(ἀνιὼν, that which goes up, i.e., up-stream with the positive current), and that moving to the kathode the *kation* (κατιὼν, that which goes down).[1] It may be noted that, although the other terms have their modern meaning, the *ion* of Faraday had scarcely the modern significance.

Faraday distinguished between *primary and secondary products* of electrolysis.[2] The primary products are deposited as such at the electrodes, e.g., hydrogen from acids, silver from silver salts. In early experiments the metals were thought to be produced by reduction by nascent hydrogen, regarded as the primary product; this was replaced by the theory that metals were primary products by Hisinger and Berzelius,[3] their theory being accepted by Davy, but rejected by Faraday.[4] This view is now accepted. The secondary products are those formed by interaction of the primary products with the solution or electrodes. When sulphuric acid is electrolyzed, the SO_4 liberated reacts with water:

$$SO_4 + H_2O = H_2SO_4 + O.$$

The theory of the constitution of acids which represents sulphuric acid as $H_2.SO_4$ and not $H_2O.SO_3$ is due to Daniell,[5] who pointed out that in the electrolysis of sodium sulphate, besides soda and sulphuric acid, hydrogen and oxygen are also liberated, so that the current appears to do twice as much work in this case as it does in the electrolysis of water or hydrochloric acid, where only one set of products is formed. The hydrogen and oxygen in the first case can then be represented as secondary products, in the formation of which the current plays no part:

$$2Na + 2H_2O = 2NaOH + H_2; \qquad SO_4 + H_2O = H_2SO_4 + O.$$

Faraday's Laws of Electrolysis: As a result of a long series of researches,[6] Faraday was able to summarize the quantitative results of electrolysis in two very simple laws:

1. *The amount of chemical action is proportional to the quantity of electricity which has passed through the electrolyte.*
2. *Ions are liberated by the same quantity of electricity in the proportions of their chemical equivalents.*

Thus: *the quantity of electricity which liberates one gram equivalent of an ion is always the same.* It is called the *faraday*, denoted by F, and the value now accepted is 96,500 coulombs.[7]

The weight z of ion liberated by one coulomb is called the *electrochemical*

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[1] Expt. Res., 7th Series, 195, the names are due to Whewell; Daneel, Elektrochemie, i, 62 (1911).

[2] Expt. Res., 7th Series, 218.

[3] *Ann. Chim.*, **51**, 174 (1804).

[4] Expt. Res., 7th Series, 219.

[5] *Phil. Trans.*, **129**, 97 (1839); **130**, 209 (1840); **134**, 1 (1844).

[6] Expt. Res., 5th Series, 145; 7th Series, 195.

[7] Washburn and Bates, *J. Am. Chem. Soc.*, **34**, 1341 (1912); Bates, *ibid.*, **34**, 1515 (1912) Bates and Vinal, *ibid.*, **36**, 916 (1914), Vinal and Bovard, *ibid.*, **38**, 496 (1916).

equivalent, it is the chemical equivalent divided by F:

$$z = M/yF,$$

where M = molar, or atomic, weight; y = valence. The weight w of ion deposited by a current of I amperes flowing for t seconds is:

$$w = Izt = IMt/yF.$$

The value of F is based on the electrochemical equivalents of silver and (most recently) of iodine.[1]

An accurate value of F and a reliable method permit of accurate measurement of current by the electrochemical method.

As a result of numerous experiments Faraday's law is found to be exact, with an accuracy of 0.01 per cent in the best cases. The relation is independent of current strength (when all secondary effects are eliminated), and holds in the case of different solvents,[2] or even in the absence of solvent (fused salts).[3] The law is probably strictly exact.

The Electronic Charge: The exact proportionality between charge and mass of an ion leads almost necessarily to the assumption, made by Helmholtz[4] and Maxwell,[5] that the current is carried convectively by the ions, each of which is associated with a fixed charge, the unit charge being that on a univalent ion, and the charges on other ions being whole multiples of this unit charge. Faraday[6] had suggested that "if we accept the atomic theory . . . the atoms of bodies which are equivalents to each other in their ordinary chemical action have equal quantities of electricity naturally associated with them," but he straightway throws doubt on this hypothesis. Erman[7] and R. Kohlrausch[8] suggested that ions are charged electrically. Hittorf[9] pointed out that salts, the constituents of which were regarded as having the most powerful affinities, are just those substances which conduct best in solution (e.g., KCl), whilst those exhibiting weaker affinities (e.g., $HgCl_2$) are much less conducting.

On Helmholtz' theory, the fundamental ionic charge, ϵ, must be equal to F/N_0, where N_0 is the number of molecules per mol. G. J. Stoney[10] named this unit charge the *electron*, and made a rough estimate of its magnitude from the value of N_0 given by the kinetic theory of gases. Recent progress has enabled the determination of N_0 to be made with an accuracy of about 0.1 per cent, as explained in another part of this book, so that the value of the electronic charge can be determined with similar accuracy. In practice it is better to invert the calculation, starting with the value of the electronic charge determined by Millikan,[1] viz., $4.774\ (\pm\ 0.005) \times 10^{-10}$ electrostatic units $= 3.33442 \times 10^{-10} \times 4.774 \times 10^{-10} = 15.9188 \times 10^{-20}$ coulombs. Then: $N_0 = 96{,}500/15.9188 \times 10^{-20} = 6.06 \times 10^{23}$, which is probably the most exact value of the Avogadro constant known.

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[1] For literature see previous chapter.

[2] Kahlenberg, *J. Phys. Chem.*, **4**, 349 (1900); Speranski and Goldberg, *J. Russ. Phys. Chem. Soc.*, **32**, 797 (1900).

[3] Lorenz, *Z. anorg. Chem.*, **23**, 97 (1900); Helfenstein, *ibid.*, **23**, 255 (1900); Auerbach, *ibid.*, **28**, 1 (1901); Lorenz, Elektrolyse geschm. Salze, ii, 91 ff.; Richards and Stull, *Proc. Am. Acad.*, **38**, 409 (1902); *Z. physik. Chem.*, **42**, 621 (1903), fused $AgNO_3$ with KNO_3 and $NaNO_3$ to 1 part in 20,000. Pressures up to 1500 atm. do not affect the value of F, Cohen, *Z. Elektrochem.*, **19**, 132 (1913).

[4] *Ann. Physik*, **11**, 737 (1880).

[5] Treatise on Electricity, 1881, Art. 255.

[6] Expt. Res., 1834, 7th Series, 256.

[7] *Gilbert's Ann.*, **8**, 197 (1801).

[8] *Ann. Physik*, **97**, 397 (1856).

[9] See under "Migration of Ions."

[10] *Proc. Dublin Soc.*, **3**, 51 (1881).

The electronic charge is capable of independent existence; it always has a negative charge, so that a negative ion is one having an excess, and a positive ion one having a defect, of electrons, as compared with the neutral atom. A positive electron in the same sense does not exist, since although the mass of the negative electron is only 1/1848 that of the lightest atom (hydrogen), the smallest positive charge known, equal but opposite in sign to the negative electron, is the hydrogen ion, or, according to the prevalent theory of atomic structure, the positive nucleus of the hydrogen atom, produced from the latter by removal of the orbital electron. This fundamental positive charge is now called the *proton*.[2]

In metallic conduction, the metal is assumed to consist of free electrons and positive ions of metal, and the electrons only move, in the opposite direction to the conventional current. In electrolytes, both positive and negative charges move in association with ions, but the current is not usually carried equally by both ions.[3]

Theory of Electrolytic Dissociation: It is but a step from the considerations advanced to the assumption that ions move in a state of freedom, but the actual order of discovery reversed this procedure, and the electrolytic ions were postulated before it was possible to demonstrate the existence of free electrons. Grove,[4] from experiments on the gas battery, assumed that in the separation of hydrogen and oxygen from water no decomposition of the water molecule occurred. Williamson [5] assumed an exchange of radicals in solutions of mixed salts; he made the assumption that, in a solution of hydrochloric acid, exchange occurs between H and Cl atoms in different molecules. It would perhaps be reading too much into his speculations to assume that they foreshadowed the theory of electrolytic dissociation. Clausius [6] adopted Williamson's theory of interchange of radicals, on kinetic grounds, but he, also, assumed it to take place to a very small extent only. This agreed, as he pointed out, with the fact that a very small E.M.F. only is required to electrolyze silver nitrate between silver electrodes, so that practically no work was used up in splitting up molecules.

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[1] The Electron, 1917; *Phys. Rev.*, **2**, 109 (1913), *Phil. Mag.*, **34**, 1 (1917), Perrin, Les Atomes, 1921 (Eng. tr. 1923), Chaps. III and IV

[2] According to Aston, Isotopes, p. 92, the name was suggested by Rutherford at the British Association Meeting in 1920.

[3] See "Migration of Ions." In some cases practically all the current is carried by one ion, and in solutions of alkali metals in non-aqueous solvents, it may be carried by free electrons.

[4] *Phil. Mag.*, **27**, 348 (1845).

[5] *Ann. Chem.*, **77**, 37 (1851); *J. Chem. Soc.*, **4**, 110 (1852).

[6] *Ann. Physik*, **101**, 338 (1857).

Arrhenius[1] first assumed that salts in solution are *extensively* broken up into ions, i.e., *electrolytically dissociated*, or *ionized*. In very dilute solutions the ionization, which increases with the dilution, becomes in many cases practically complete. This theory explained the abnormally large osmotic pressures of solutions of electrolytes, and a similar explanation was put forward independently by Planck[2] from another point of view. In both cases it was recognized that, if the laws of dilute solution are to remain valid, an increase in the number of particles must have occurred in the solution of an electrolyte.

This theory, naturally, met with little support from the conservative chemist, but although many attempts to bring forward really destructive objections have been made, the development of physics has put the theory on a very solid foundation. In its most modern form, in fact, the theory assumes even the solid salt to be made up of ions, and some physicists would go so far as to assume complete ionization of salts both in the solid and dissolved forms. The examination of crystals by X-rays has indicated that sodium chloride, for example, consists not of NaCl molecules but of Na^+ and Cl^- ions arranged in a space lattice, and in solution such a crystal would simply fall apart into its ions.[3] Such a constitution of salt crystals is in agreement with their optical and elastic properties, and with the theories of atomic structure.

The notation used in representing ions, due to Ostwald,[4] is to write the symbol of the ion, with a number of dots or dashes for the number of units of positive or negative charge, respectively, carried by the ion. This number represents at the same time the valence of the ion. Thus

$$H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4' \rightleftharpoons H^{\cdot} + H^{\cdot} + SO_4''$$

represents the progressive ionization of sulphuric acid on the assumption that ionization increases with dilution and that ions and molecules are in chemical equilibrium. Ionization may occur in stages, and except at high dilution, usually the first stage only is appreciable. The sum of the positive and negative charges on the ions is always zero, since the solution is electrically neutral as a whole. The charged ions in electrolysis are attracted to the electrodes of opposite sign, and give up their charges. The uncharged particles may be capable of independent existence, or may form molecules of the same composition, or may react with the solvent to form secondary products.

Whether ionization is due simply to the falling apart of the two parts of a molecule on solution, or whether it is due to the previous interaction between

[1] *Z. physik. Chem.*, 1, 631 (1887); Harper's *Science Series*, vol. 4, p. 47.

[2] *Ann. Physik*, **32**, 462 (1887); *Z. physik. Chem.*, 1, 577 (1887).

[3] Cf. B. Cabrera, *Anal. Fis. Quim.*, **16**, 186 (1918).

[4] Grundriss der Allgemeinen Chemie, Leipzig, 1909, p. 441; cf. Walker, *Chem. News*, **84** 162 (1901).

solute and solvent,[1] cannot be said to have been definitely decided. Kendall[2] *adopts the second supposition, and concludes that two non-associated substances which are chemically inert do not give a conducting solution. Ionization is always accompanied by interaction between solute and solvent. Tendency to compound formation (solvation) and ionization are parallel, and ionization in general is supposed to be preceded by compound formation.* This union of the so-called "chemical" theory of solution and the theory of electrolytic dissociation is interesting and promising, but it does not yet rest on sufficient evidence on the non-aqueous side.

Evidence for the Theory of Electrolytic Dissociation: The theory of Arrhenius has a good deal of experimental evidence which may be called upon in its support.[3] This may be summarized as follows:

1. The qualitative reactions of such substances as KCl and $KClO_3$ indicate that the reactions of chlorides are due to the chloride ion and not merely to chlorine present in the molecule. $KClO_3$ gives the ions $K^{\cdot}$ and ClO_3'. In quantitative analysis, also, the effects of excess of reagent are explained by the theory (see "Solubility Product").

2. The additive properties of solutions are clearly explained by the theory. Valson showed that the surface tensions [4] and densities [5] of salt solutions could be regarded as the sum of three separate magnitudes, characteristic of the solvent, the metallic constituent (kation), and the acid radical (anion). Other additive properties were shown to follow the same rule, indicating the separate existence of ions in the solution,[6] notably the heat of neutralization of a strong acid by a strong base in dilute aqueous solutions. This is always 13.65 kgm. cal., the heat of formation of water from ions: $H^{\cdot} + OH' = H_2O$, e.g., $H^{\cdot} + Cl' + Na^{\cdot} + Cl' = Na^{\cdot} + Cl' + H_2O + 13.65$ kgm. cal. This result has been confirmed *exactly* by the refined experiments of T. W. Richards and Rowe,[7] who find that the heats of neutralization of potassium, sodium and lithium hydroxides by hydrochloric, hydrobromic, hydriodic and nitric acids at 20°, when extrapolated *through a short range* to infinite dilution, vary only between the limits 13.62 and 13.69 kgm. cal.

3. The calculation of the diffusion coefficient of a salt from the conductivity, and the effect of chlorides on the diffusion of hydrochloric acid,[8] are in perfect agreement with the theory.

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[1] Ciamician, *Z. physik. Chem.*, **69**, 96 (1909).

[2] *Proc. Nat. Acad. Sci.*, **7**, 56 (1921); Kendall and Booge, *J. Am. Chem. Soc.*, **39**, 2323 (1917); Kendall and Gross, *ibid.*, **43**, 1416, 1426 (1921); Kendall, Davidson and Adler, *ibid.*, **43**, 1481 (1921); Kendall and Andrews, *ibid.*, **43**, 1545 (1921); Partington, *J. Chem. Soc.*, **97**, 1158 (1910).

[3] Arrhenius, Faraday Lecture, *J. Chem. Soc.*, **105**, 1414 (1914), Gibbs Address, *J. Am. Chem. Soc.*, **34**, 353 (1912); *Trans. Farad. Soc.*, **15**, 10 (1919), cf. Dhar, *Z. Elektrochem.*, **22**, 245 (1916).

[4] *Ann. Chim. Phys.*, **20**, 361 (1870).

[5] *Compt. rend.*, **73**, 441 (1874).

[6] Ostwald, Lehrbuch, vol. 1, "*Salzlösungen*"

[7] *J. Am. Chem. Soc.*, **44**, 684 (1922); cf Hess, *Ann Physik*, **50**, 385, **52**, 97 (1842).

[8] Arrhenius, *Z. physik. Chem.*, **10**, 74 (1892).

4. The colors of solutions at high dilution should be additively composed of those of the solvent and the two ions. With an uncolored solvent, such as water, and one ion uncolored, all solutions of salts with a common colored ion, e.g., all permanganates, should show the same absorption spectrum. This was confirmed by Ostwald.[1]

5. The experimental fact that the equivalent conductance, Λ, increases with dilution, but ultimately approaches a limiting constant value at high dilution, is very simply explained by the theory (see later).

6. The excellent agreement of Ostwald's dilution law (*q v.*) for weak acids and bases is strong evidence for the theory The disagreement of strong electrolytes is a difficult problem, but no suggestion towards an explanation of the deviation has been made which does not assume electrolytic dissociation in some form or other. At very high dilutions the law probably holds even for strong electrolytes.[2]

7. The abnormal freezing point depressions for aqueous solutions of salts can be satisfactorily explained by the theory. Noyes and Falk[3] show that for solutions not more concentrated than 0 1 *n*, the ionization calculated from the freezing point does not differ from that calculated from conductivity by more than 2 per cent in the case of electrolytes containing two univalent ions. Hygroscopic salts with bivalent kations show greater depressions than calculation requires. In a valuable series of papers Noyes and Falk have collected the data for freezing point lowering,[4] transport numbers,[5] and conductivity[6] of aqueous solutions. In the last paper the values of the ionization of the salts at various dilutions are given. The ionization is not an additive property with respect to the ion constituents, and is not related to the mobilities of the ions. The ionizations at 18° and 25° agree within the limits of experimental error.

8. The velocity of reaction shows that those acids are strongest which are most conducting in solution, and Ostwald thought that the catalytic activity of acids in hydrolyzing methyl acetate was proportional to the conductivity. Arrhenius in 1889 showed that the activity was proportional to the $H^{\cdot}$ ion concentration, but recent work has modified this view.

Specific, Equivalent, and Molar Conductance: The relation between resistance, current, and pressure (potential difference between the ends of a conductor) was summarized by G. S. Ohm[7] in the well-known law. If *R* is the resistance, E the electric pressure, and I the current, then $E = kIR$, where k is a factor depending only on the choice of units and can be made equal to unity. The *International Ohm* is the unit of resistance and is defined as the *resistance offered to an unvarying current by a column of mercury at the temperature of melting ice, 14.4521 grams in mass, 106.300 cm. in length,* and of constant cross section. The *International Ampère* is the unit of current and is defined as the unvarying electric current which when passed through a solution of silver nitrate in water, in accordance with specified conditions, deposits silver at the rate of 0.00111800 gram per second. The *International Volt,* the unit of electric pressure, is then defined by Ohm's law as the electric pressure which, when steadily applied to a conductor the resistance of which is one International Ohm, will produce a current of one International Ampère.

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[1] *Z. physik. Chem*, **9**, 579 (1892), cf however papers by Houstoun, Anderson, Brown, Cochrane and Gray in *Proc. Roy. Soc. Edin*, 1910 1913 Wright, *J Chem. Soc*, **103**, 528, (1913); **105**, 669 (1914), finds that strong acids exert the same absorptive power on light as their salts, whilst weak acids (little dissociated) often show great variations, as would be expected. See also the interesting papers of Schafer, *Z anorg Chem*, **97**, 285, **98**, 70 (1919); *Z. physik. Chem*, **93**, 312 (1919), and Hantzsch, *Ber*, **50**, 1422 (1917).

[2] Washburn and Weiland, *J. Am. Chem Soc*, **40**, 131, 151 (1918)

[3] *J. Am. Chem. Soc.*, **34**, 454 (1912).

[4] *J. Am. Chem. Soc*, **32**, 1011 (1910).

[5] *Ibid.*, **34**, 454 (1912).

[6] *Ibid.*, **33**, 1436 (1911).

[7] Die galvanische Kette, mathematisch bearbeitet, Berlin, 1827, he does not use the term "resistance," but speaks of "reduced lengths" of conductors

If a conductor of length L cm. and uniform cross section A sq. cm. has a resistance R, then $r = RA/L$ is called the *specific resistance,* or *resistivity,* of the material of the conductor. The *conductance* is the reciprocal of the resistance, and the *specific conductance,* or *conductivity,* of the material is

$$\kappa = 1/r = L/RA.$$

Thus

$$R = Lr/A = L/\kappa A.$$

If a liquid is contained in an electrolytic cell, and if $\kappa = C/R$, where R is the resistance of the cell, then C is called the *cell constant.* It may be determined with a liquid of known conductivity in the cell.[1]

If the cell is a cylinder of length L and section A, and if the electrodes fill the section completely, then $C = L/A$.[2]

As standard liquids Kohlrausch[3] recommends a number of solutions, but in many cases these are suitable only for approximate work. The standard is normal potassium chloride solution made up from 74.555 grams of pure KCl weighed in air and diluted to 1 litre at 18°. This should have a density of 1.04492 at 18°.[4] $\kappa = 0.09822$ at 18°.

Other solutions of KCl prepared by dilution of the normal are $n/10$, $n/50$ and $n/100$, with conductivities of 0.01119, 0.002397 and 0.001225, respectively, according to Kohlrausch.

Equivalent Conductance: The conductivity of a solution depends on its concentration. The *equivalent conductance,* Λ, is defined as the conductivity divided by the concentration, η, in equivalents *per cc.* (not per litre), $\Lambda = \kappa/\eta$.

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[1] The cell constant applies only to a particular temperature, Washburn, *J. Am. Chem. Soc.*, **38**, 2431 (1916). Schlesinger and Read, *ibid.*, **41**, 1727 (1919), state that C should be determined with solutions covering the whole range of conductances to be measured with the cell.

[2] Kohlrausch and Holborn, Leitvermogen der Elektrolyte, 1916, p. 12.

[3] Leitvermögen, p. 76 ff.

[4] Washburn, *loc. cit.*, determines cell constants with a solution of 7.43000 grams KCl in 1000 grams of *solution* (weights in air); κ at 25° = 0.01288; at 0° $\kappa = 0.00715$. Kraus and Parker, *J. Am. Chem. Soc.*, **44**, 2422 (1922), propose to take 0.1 KCl with $\kappa = 0.011203$ at 18° from Kohlrausch and Maltby's results, and find then κ at 25° = 0.0128988. Graetz in Winkelmann's Physik, IV, i, 331, gives weights *in vacuo*.

The reciprocal of concentration, $\varphi = 1/\eta$, is called the *dilution*. The name equivalent conductance is due to Lenz.[1]

The *molar conductance*, μ, used by Ostwald, is defined as the conductivity divided by the concentration c in mols. per litre: $\mu = \kappa/c$. In making use of the values of μ given by Ostwald and by H. C. Jones and his co-workers it is necessary to remember that they are based on the Siemens resistance unit, and require multiplication by 1.066 to reduce to reciprocal ohms. They have been recalculated by Kohlrausch.[2]

If a volume of solution containing one equivalent of solute is poured into a cell formed of parallel plates one centimeter apart, the conductance will be equal to the equivalent conductance. For, the liquid may be divided into φ cubical cells each of unit volume, and each will have the specific conductance κ. Thus the total conductance will be: $\kappa\varphi = \kappa/\eta = \Lambda$.

For good conductors the influence of the conductivity of the solvent itself may be neglected, but at high dilutions it is usual to subtract the conductivity of the solvent, κ_0, from the total conductivity, and to define Λ as $(\kappa - \kappa_0)/\eta$.[3] Ostwald[4] in 1885 pointed out that this leads to impossible values in the case of acids and bases in dilute solutions, and suggested that this was due to chemical interaction between the solute and impurities in the water. This makes the determination of equivalent conductances of acids and bases in very dilute solutions a matter of very considerable difficulty.

The values of Λ so far determined, with the exception of very recent ones, are collected in Kohlrausch and Holborn's Leitvermogen der Elektrolyte. More recent determinations have been made by Noyes and Johnston,[5] Hunt,[6] Sloane,[7] Kato,[8] Paine and Evans,[9] Wormann,[10] Muller,[11] H. C. Jones and his co-workers,[12] Tucker,[13] Sachanov,[14] Bray and Hunt,[15] de Lenaizan and Maury,[16]

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[1] *Ann. Physik*, **160**, 425 (1877).

[2] Leitvermogen, see also Whetham, Theory of Solution, 1902, 107 ff., it must also be remembered that different values of the ohm, atomic weights, and concentration units, all affect the results. On correction for atomic weights see Kohlrausch, *Z. physik. Chem.*, **72**, 43 (1910).

[3] Arrhenius, *Bih. Svensk. Akad. Handl.*, **8**, Nr. 13 (1884), Kohlrausch, *Ann. Physik*, **26**, 161 (1885). This procedure will be discussed later.

[4] *J. prakt. Chem.*, **140**, 300 (1885).

[5] *J. Am. Chem. Soc.*, **31**, 987 (1909).

[6] *Ibid.*, **33**, 795 (1911).

[7] *Ibid.*, **32**, 946 (1910), at 0°.

[8] *Mem. Coll. Sci. Eng. Kyoto*, i, 332 (1908) (high temp.).

[9] *Proc. Cambr. Phil. Soc.*, **18**, 1 (1914).

[10] *Ann. Physik*, **29**, 141, 623 (1909).

[11] *Bull. Soc. Chim.*, **11**, 1001 (1912).

[12] *Am. Chem. J.*, **42**, 520 (1909), **44**, 159, 187, 508 (1910), **46**, 56, 368 (1911), **48**, 320, 500 (1912); **50**, 1 (1913), **49**, 207 (1913); *J. Am. Chem. Soc.*, **37**, 2626 (1915); *Z. physik. Chem.*, **46**, 244 (1904).

[13] *Proc. Phys. Soc. London*, **25**, 11 (1913).

[14] *Z. Elektrochem.*, **19**, 588 (1913).

[15] *J. Am. Chem. Soc.*, **33**, 781 (1911).

[16] *Compt. rend.*, **173**, 227 (1921).

Lorenz and Posen,[1] Werner and Miolati,[2] Svanberg,[3] and Rabinowitsch.[4] Older work is that of Ostwald on organic acids[5] and of Bredig on organic bases.[6]

Experimental Determination of Electrolytic Conductivity: Many attempts were made to determine conductances of solutions before a satisfactory method was found. Apart from errors due to insufficient attention to the effect of temperature, the chief error in older work was that caused by polarization of the electrodes. When finite deposition of ions on the electrodes occurs, a cell is set up, the electromotive force of which opposes that driving current through the solution. Unless a pressure in excess of the force of polarization is applied to the terminals of the cell no current flows, whilst according to Ohm's law the smallest applied pressure should lead to the corresponding current. As a final result of experiments it was shown that, provided polarization was eliminated, Ohm's law is accurately followed, and electric pressure and current vanish together.

Direct current measurements were made by Horsford,[7] who passed a current between two electrodes in a rectangular trough, and then moved them closer together. The current increased, but by inserting a wire in series it could be restored to its original value. Horsford assumed that the effect of polarization was the same in both positions of the plates, and the resistance of the wire then gave that of a column of liquid equal in length to the distance through which the plates were moved nearer together. The method was improved[8] by using electrodes of the metal present in solution, when polarization was reduced.[9] Further improvements were made by Beetz[10] who used amalgamated zinc plates in zinc sulphate solution, when polarization was almost eliminated. In the method due to Fuchs[11] a constant current is passed through a solution and the drop in potential between two points measured by secondary electrodes connected with an electrometer. Bouty used zinc rods in solutions of zinc sulphate as subsidiary electrodes; recent experimenters (who appear to think the method new) use calomel (Newbery) or hydrogen (Marie and Noyes) electrodes. The method is capable of some accuracy, but has no special advantages.

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[1] *Z. anorg. Chem.*, **96**, 81 (1916).

[2] *Z. physik. Chem.*, **12**, 35 (1893); **14**, 506 (1894).

[3] *Medd. K. Vetenskapsakad. Nobel Inst.*, **3**, No. 26 (1918).

[4] *Z. physik. Chem.*, **99**, 338, 417 (1921).

[5] *Z. physik. Chem.*, **3**, 170, 241, 369 (1889).

[6] *Ibid.*, **13**, 289 (1894). Many organic acids were measured by Wegscheider, *Monatsh.*, **37**, 219 (1916). See Soudder, Electrical Conductivity and Ionization Constants of Organic Compounds, London, 1914, and the collected monographs of Jones and Noyes in the Carnegie Institute Reports. Work at high temperatures, see Noyes, Melcher, Cooper and Eastman, *Z. physik. Chem.*, **70**, 335 (1910). A complete, critical, set of tables of conductivity results is still required.

[7] *Ann. Physik*, **70**, 238 (1847); Malmstrom, *Z. physik. Chem.*, **22**, 331 (1897); Christiansen, *Chem. Soc. Abstr.*, ii, 9 (1921); Morgan and Hildburgh, *J. Am. Chem. Soc.*, **22**, 304 (1900).

[8] G. Wiedemann, *Ann. Physik*, **99**, 177 (1856).

[9] Cf. W. Schmidt, *Ann. Physik*, **107**, 539 (1859); R. Lenz, *Bull. Acad. Petersb.*, **22**, 439 (1876); *Ann. Physik*, **160**, 425 (1877).

[10] *Ann. Physik*, **117**, 1 (1862); Tollinger, *ibid.*, **1**, 510 (1877); Paalzow, *ibid.*, **136**, 489 (1869); Berggren, *ibid.*, **1**, 499 (1877); Freund, *ibid.*, **7**, 44 (1879).

[11] Fuchs, *Ann. Physik*, **156**, 156 (1875); Bouty, *J. de Phys.*, **3**, 325 (1884); **6**, 5 (1887); *Ann. Chim. Phys.*, **14**, 36, 74 (1888); Sheldon, *Ann. Physik*, **34**, 122 (1888); Rasehorn, *Diss.*, Halle (1889); Newbery, *J. Chem. Soc.*, **113**, 701 (1918); Marie and W. A. Noyes Jun., *J. Am. Chem. Soc.*, **43**, 1095 (1921).

Stroud and Henderson[1] used two narrow tubes of equal diameter but unequal lengths as two arms of a Wheatstone's bridge, the other two being composed of equal coils. Resistance was added to the shorter tube till the bridge was balanced. The assumption is made that the effects of migration and polarization are equal in the two tubes, and the added resistance is then equal to the resistance of the liquid column equal in length to the difference between the two tubes.

Beetz[2] eliminated electrodes altogether by making use of currents induced in the liquid by a moving magnet.

The most satisfactory method of eliminating polarization is the use of alternating currents of sufficiently high frequency.[3] This is combined with the use of electrodes coated with platinum black,[4] which expose a large surface and so reduce as far as possible the surface density of the ions deposited, to which the E.M.F. of polarization is proportional. The platinum is deposited on the electrodes from a solution of 1 gram of chloroplatinic acid and 0.008 gram of lead acetate in 30 cc. of water. The electrodes are immersed in this and current from two accumulators passed backwards and forwards between the electrodes, with reversals every few minutes. A resistance is inserted so that a gentle evolution of gas occurs, and a fine deep black coating of platinum, free from lead, is deposited. The electrodes are then immersed for some hours in warm distilled water, frequently changed, to remove adsorbed salt. If the electrodes are allowed to dry, they are afterwards wetted with difficulty: they may then be washed with absolute alcohol and then with water, but are best kept standing in water. In the case of alcoholic solutions, and solutions of cobaltammine salts[5] oxidation may occur, and unplatinized platinum is then used. Whetham[6] reduces adsorption of salts from dilute solutions by heating the platinized electrode to redness, when a grey surface is obtained, non-adsorbent, and sufficient to prevent polarization. In accurate work with a series of solutions, the dilute ones should first be used, as, otherwise, salt adsorbed from the stronger solutions tends to come out again into the dilute ones. The electrodes after a time require replatinizing. The preparation of the platinum foil for the electrodes, which should be free from iron and calcium, is described by Kohlrausch.[1]

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[1] *Phil. Mag.*, **43**, 19 (1897), *Proc. Phys. Soc. London*, **15**, 13 (1897), Watson, Practical Physics, London (1908), p. 481.

[2] *Ann. Physik*, **117**, 1 (1862), Guthrie and Boys, *Phil. Mag.*, **10**, 328 (1880).

[3] F. W. Kohlrausch and Nippoldt, *Gotting. Nachr.*, 415 (1868), 1 (1869), *Ann. Physik*, **138**, 280, 370 (1869), Smith and Moss, *Proc. Phys. Soc. London*, **25**, 133 (1913), Taylor and Acree, *J. Am. Chem. Soc.*, **38**, 2396, 2403, 2415 (1916), Taylor and Curtis, *Phys. Rev.*, **6**, 61 (1915).

[4] F. W. Kohlrausch and Grotrian, *Gotting. Nachr.*, 405 (1874), *Ann. Physik*, **154**, 1, 215 (1875); Lummer and Kurlbaum, *Verh. Deut. Phys. Ges.*, **14**, 56 (1895), Wien, *Ann. Physik*, **58**, 57 (1896).

[5] Partington. *J. Chem. Soc.*, **99**, 1937 (1911), Lorenz and Posen, *Z. anorg. Chem.*, **96**, 81 (1916).

[6] *Phil. Trans.*, **194**, 321 (1900). Kellner, *Ann. Physik*, **57**, 79 (1896).

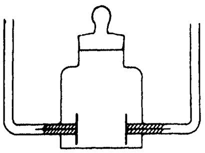
FIG. 2. Conductivity Cell

Conductivity Cells: Numerous types of conductivity cell have been described,[2] but for ordinary measurements the writer finds the cell shown in Fig. 2 satisfactory. It can be made in different sizes, with the space between the electrodes suited to the electrolyte. Cells with sliding electrodes, or electrodes easily distorted, should be avoided. The electrodes are of stout sheet platinum, with platinum wires welded on and covered with glass inside the cell. The side tubes contain a few drops of mercury to make contact with copper wires, prolonged by rubber tubing so that the cell may be placed in the thermostat. The cell is filled almost to the stopper, which is then firmly fitted and covered with a little Faraday cement.

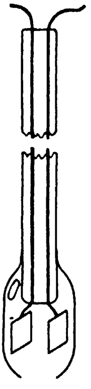
FIG. 3. Dipping Electrode Cell

Dipping electrodes, Fig. 3, are often convenient. The platinum wires and electrodes must be stout, so that they are not displaced by the liquid. All cells should be of good glass; Jena 16 III is not attacked by water and seals directly into platinum. For special work metal cells have been used.[3] The design of conductivity cells has been considered in detail by Washburn.[4] The area of cross section must not be less than a fixed value determined by: (i) the audibility current in the telephone used as indicator, (ii) the conductivity of the liquid having the maximum desired resistance in the cell, (iii) the density of the liquid, (iv) the heat capacity and temperature coefficient of resistance of this liquid, and (v) the percentage accuracy demanded in the measurement. It does not depend on the distance between the electrodes. When the heating effect of the current is brought into consideration, the resistance of the slide wire and telephone and the time required to make a bridge setting also come in. Washburn has devised certain types and sizes of cell, adapted to measurements with (*a*) water or very dilute solutions, (*b*) dilute solutions, (*c*) concentrated solutions. As finally set up,[1] these are shown in Fig. 4. Those of type (*a*)

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[1] Leitvermögen, p. 11; platinized glass electrodes, see Meillère, *J. Pharm. Chim.*, **21**, 311 (1920); effect of platinizing, see Taylor and Acree, *J. Am. Chem. Soc.*, **38**, 2415 (1916); the effect of frequency on the apparent resistance decreases as the area of surface exposed increases. There is a specific relation between the electrolyte, the electrode material and surface, and the change of capacity and resistance with frequency of the alternating current.

[2] Kohlrausch, Leitvermögen, p. 12 ff.; Rice, *J. Ind. Eng. Chem.*, **12**, 1202 (1920); Miles, *Proc. Roy. Soc. Edinb.*, **35**, 138 (1915); Acree and Robertson, *J. Phys. Chem*, **19**, 381 (1915), Robbins, *J. Am. Chem. Soc.*, **39**, 646 (1917); theory of design of cells, Washburn, *J. Am. Chem. Soc.*, **38**, 2431 (1916); Leeds and Northrup Catalog No. 48 (1919), other cells, J. and G. E. Gibson, *Proc. Roy. Soc. Edinb.*, **30**, 254 (1910); Hill and Sirkar, *Proc. Phys. Soc. London*, **83**, 130 (1909) (wax cell for HF).

[3] McBain and Taylor, *Z. physik. Chem.*, **76**, 179 (1911) (silver); Bowden, *J. Chem. Soc.*, **99**, 192 (1911) (silver); Noyes and Coolidge, *Z. physik. Chem.*, **46**, 323 (1903) (platinum); Kato, *Mem. Coll. Sci. Eng. Kyoto*, i, 332 (1908) (platinum).

[4] *J. Am. Chem. Soc.*, **38**, 2436 (1916).

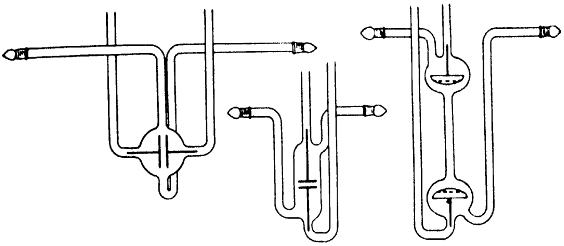

FIG. 4*a* FIG. 4*b* FIG. 4*c*

FIGS. 4*abc*. Conductivity Cells Washburn Types

have electrodes which are unplatinized, those of type (*b*) have lightly platinized, and those of type (*c*) heavily platinized, electrodes. The bridge leads are connected with the cell leads by a pair of mercury cups dipping into the bath containing the cell, to prevent flow of heat between the cell plates and the room. The cells are of the pipette type, the ends of the inlet tubes being covered with ground glass caps

Jena glass is sufficiently resistant for all solutions made up and [2] handled in air; in such cells conductivity water with a specific conductance of 0.21 $\times 10^{-6}$ ohm^{-1} can be kept 12 hours without change, and even after several weeks does not rise above 0.6 $\times 10^{-6}$ ohm^{-1}, the contamination in this case certainly coming from the atmosphere.[3] The use of quartz cells is quite needlessly ostentatious except for the conductivity of the purest water The cells should be carefully annealed and aged before use. Large changes of temperature lead to thermal strains which alter the distance between the electrodes.

The Alternating Current: The alternating current is normally supplied by a small induction coil without a condenser, having a high frequency hammer. Such coils are specially supplied. Kohlrausch [4] gives the dimensions of the core as 8 cm. long and 1 cm. thick, of solid soft iron, on which are wound 200 turns of 0.5 mm. copper primary and 2000 turns of 0 25 mm. copper secondary. One accumulator with a resistance is sufficient. The contact hammer is the most important part; it is often necessary to replace the one supplied by a spring giving the right frequency. The contacts should be well platinized. Satisfactory results are only attained by trial and patience, but it is quite unnecessary except for the work of highest precision to use any other source of current.[1]

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[1] Leeds and Northrup Catalog No. 48 (1919), p 25 f.

[2] Kohlrausch, *Ber.*, **26**, 2998 (1893); Foerster, *ibid* , **26**, 2915 (1893).

[3] Washburn, *J. Am. Chem. Soc* , **38**, 2455 (1916).

[4] Leitvermögen. p. 26.

Stretched horizontal steel wires have been used[2] instead of hammers, and high frequency apparatus is described by Nernst.[3] These may be regarded as superseded by the valve oscillator. In the work of Washburn[4] a high frequency generator giving a pure sine wave current of single frequency was used. The Vreeland Oscillator[5] generates alternating currents having a pure sinusoidal character and a constant but controllable frequency. These are expensive. The use of a direct current with a rotating commutator and galvanometer has been recommended:[6] when it is used, the resistance must remain constant when the speed is varied, or the ratio arms of the bridge changed by a constant multiple. Hall and Adams and Miller[7] used the thermionic valve as a generator of current of high frequency. The connections are shown in Fig. 5. The condensers C_1 and C_2 control the frequency, one being of small capacity and continuously variable and the other variable in steps of 0.005 microfarad. "Generators of this type may be made to yield a current of from a few tenths of a milliampère or less to 25 ampères and with a frequency varying from half a cycle per second to 50 million cycles per second." At frequencies below 1000 cycles, a troublesome first harmonic is present. The arrangement for amplification, when a very weak current is sent through the cell, is shown in Fig. 6.[8]

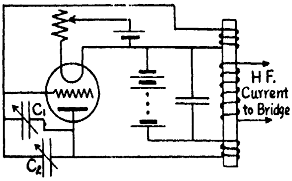

FIG. 5. Thermionic Valve Connections for Conductivity Measurements

The thermionic valve may be regarded as displacing the more expensive apparatus noticed above.[9]

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[1] Various types of current producers, Taylor and Acree, *J. Am. Chem. Soc.*, **38**, 2396 (1916); their judgment of the Vreeland oscillator may now be revised in the light of Hall and Adams' use of the valve oscillator (see below). J. C. Ghosh, *J. Am. Chem. Soc.*, **36**, 2333 (1914); **37**, 733 (1915), finds that an alternating current superposed on direct current reduces polarization; this had previously been described by Reitlinger, *Z. Elektrochem.*, **20**, 261 (1914), and by Wartenberg and Archibald, *ibid.*, **17**, 812 (1911).

[2] Melde, *Ann. Physik*, **24**, 497 (1884); Wien, *ibid.*, **42**, 593 (1891); **44**, 681 (1891); Nernst, *Z. physik. Chem.*, **14**, 622 (1894), Rubens, *Ann. Physik*, **56**, 27 (1895); Orlich, *Elektrotechn. Z.*, **26**, 502 (1903).

[3] *Ann. Physik*, **60**, 600 (1897); Cohn, *ibid.*, **21**, 646 (1884); Erskine, *ibid.*, **62**, 454 (1897); Nernst and Lerch, *ibid.*, **15**, 836 (1904).

[4] *J. Am. Chem. Soc.*, **38**, 2431 (1916).

[5] Leeds and Northrup Catalog No. 48 (1919), p. 14 f.

[6] MacGregor, *Trans. Roy. Soc. Canada*, **1**, 21 (1882); Fitzpatrick, *Brit. Ass. Rep.*, p. 328 (1886); Whetham, *Phil. Trans.*, **194**, 321 (1900); Pfleiderer, *Z. Elektrochem.*, **19**, 925 (1913).

[7] *J. Am. Chem. Soc.*, **41**, 1515 (1919).

[8] On sensitivity of telephones see Washburn, *J. Am. Chem. Soc.*, **39**, 235 (1917).

[9] Theory and descriptions of thermionic valves: De Forest, *Electrician*, **73**, 842 (1914); *Electr. World*, **65**, 465 (1914); Langmuir, *Phys. Rev.*, **2**, 450 (1913), *Gen. Electr. Rev.*, (May), 327 (1915); Armstrong, *Electr. World*, **64**, 1149 (1914); Van der Bijl, *Phys. Rev.*, **12**, 171

Current Detector: The most satisfactory instrument for the detection of alternating current in bridge measurements is the telephone,[1] introduced by Kohlrausch. For ordinary work the writer finds the old long Bell telephone usually much better than the flat type. The choice of a good telephone is essential, and some slight adjustment is often required. A common trouble is iron particles between the disc and magnets. Absolute vanishing of the sound is never attained, but a well-defined minimum should be got if all is in order. The resistance of the telephone may be about 10 ohms or less, and the remaining resistances adjusted accordingly. The use of electrodynamometers and vibration galvanometers[2] is not recommended.

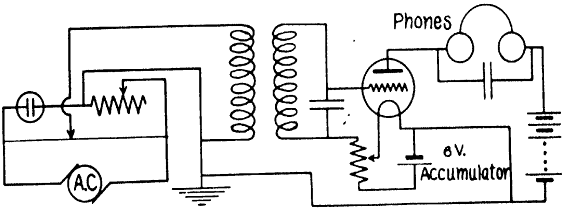

Fig. 6 Experimental Arrangement for Weak Currents

Resistance Bridge: A Wheatstone bridge arrangement of ordinary type may be used. For ordinary work a simple stretched wire of constantan or platinum-iridium, with a knife-edge tapping contact, is sufficient. The coil and telephone are connected with a plug resistance box as known resistance, and the cell, as in Fig. 7. The wire may also be wound on an ebonite or marble drum, with a wheel contact.[3] The wire must be carefully calibrated.[4] Dial resistance boxes are convenient. Nernst[5] recommends the use of standard liquid resistances of negligible temperature coefficient to balance the electrolytic cell, when the bridge arrangement is more symmetrical and sharper readings are obtained. The solution contains 121 grams of mannitol, 41 grams of boric acid, and 0.06 gram of potassium chloride per litre. Its conductivity at 18° is 0.00097 ohm.[6]

(1918); Latour, *Electrician*, 78, 280 (1916). *Circular Bur. Stand.*, 74, 200 (1918). Fleming, *Proc. Roy. Inst.*, 23, 161 (1923).

[1] Washburn and Parker, *J. Am. Chem. Soc.*, 39, 235 (1917): a precision of 1 in 10^5 can be attained with a telephone with an audibility current of 10^{-8} amp., which is reached in telephones of moderate price. Tuning to the frequency of the current is discussed. See also Rayleigh, Phil. Mag., 1894, 38, 285, 295.

[2] Kohlrausch, Leitvermogen, p. 30 f. Flat type 'phones with adjustable magnets are now obtainable.

[3] Kohlrausch, *Ann. Physik*, 11, 653 (1880); 56, 177 (1895); Leitvermogen, p. 41.

[4] Kohlrausch, Leitvermögen, p. 45. See also, for precision bridges, Leeds and Northrup Catalog No. 48 (1919), p. 21 f.

[5] *Z. physik. Chem.*, 14, 622 (1894). Magnanini, *ibid.*, 6, 58 (1890).

[6] On such solutions see numerous papers by Boeseken and co-workers. *Proc. K. Akad. Wetens. Amsterdam*, 15, 216 (1912); *Rec. Trav. Chim.*, 30, 392 (1911); 34, 96, 272 (1915).

If resistance coils are used they should be bifilar wound so as to neutralize self-inductance, but as this introduces considerable capacity in large coils (1000 ohms and over), the latter (only) should be wound by Chaperon's method,[1] i.e., in simple layers but each layer in the reverse sense to the preceding. The box should have coils of, say, 30, 70, 200, 700, 2000 and 7000 ohms. The resistance taken from the box should bring the slider to about the middle of the bridge wire in making the balance. If an electrodynamometer is used, the connections are shown in Fig. 8; one coil is put in series with the induction coil I, and the other diagonally across the bridge.[2]

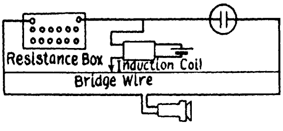

Fig. 7. Experimental Arrangement for Conductivity Measurements

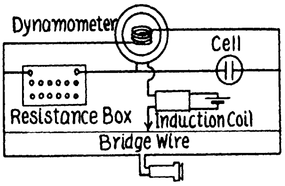

Fig. 8. Experimental Arrangement for Conductivity Measurements using Dynamometer

The method of carrying out the conductivity measurement is simply to adjust the resistance in the arm opposite the cell till the minimum sound is heard in the telephone. The bridge is then regarded as balanced. The sources of error in Kohlrausch's method have been studied by Washburn and Bell,[3] and an improved technique for solutions between 0.001 *n*. and 0.000001 *n*. evolved. A high frequency generator replaces the coil, and special resistance units in the box are made by sealing platinum wires into the ends of a glass rod and connecting them by a film of platinum deposited on the glass. A tuned telephone and an extended bridge wire are used, all measurements being made about the middle of the bridge. The precision reached with all solutions from pure water to 6 *n*. was 0.01 per cent, which can be extended to 0.001 per cent with care in most cases. In a later paper,[4] it is stated that an induction coil has a unidirectional component, and its time integral is not zero, leading to some polarization; it is also impossible to keep the frequency constant. A telephone tuned to the frequency used[5] must also be employed: various methods of tuning (mechanical, electrical and acoustical) are described. The paper condensers used by Kohlrausch (see later) are unsuitable for very

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35, 211, 309 (1916); **36**, 167 (1916); *Proc. K. Akad. Wetens. Amsterdam*, **18**, 1647 (1916); **21**, 907 (1919); *Rec. Trav. Chim.*, **37**, 130, 144, 162, 165, 179 (1918), **39**, 178 (1920); **40**, 568, 574 (1921).

[1] *Compt. rend.*, **108**, 799 (1889); *J. de Phys.*, **9**, 481 (1890). Curtis and Grover, *Bull. Bureau Stand.*, **8**, 514 (1911) (improved method).

[2] Cf. Acree and Taylor, *J. Am. Chem. Soc.*, **38**, 2403, 2415 (1916).

[3] *J. Am. Chem. Soc.*, **35**, 177 (1913).

[4] Washburn, *J. Am. Chem. Soc.*, **38**, 2431 (1916).

[5] *Ibid.*, **39**, 235 (1917).

accurate work. They are replaced by air or mica condensers.[1] A frequency of about 1000 per sec. is recommended.

Conductivity Water: Very pure water is essential for conductivity work. The same applies, of course, to other solvents used The purest water was obtained by Kohlrausch and Heydweiller[2] and had a specific conductance of only 0.043×10^{-6} ohm^{-1} at 18°, but very special precautions had to be used to obtain only a few cc. of this water, and the operation has never been repeated with success since.[3]

Water was distilled backwards and forwards forty-two times in a vacuum at a low temperature, and collected directly in a glass conductivity cell which had been kept ten years filled with conductivity water to remove traces of soluble matter from the glass. In air, the conductivity of the best water rises to at least 0.7×10^{-6}, chiefly owing to dissolved carbon dioxide, and a good water for general use may be taken as one about 1×10^{-6}. Water prepared and stored in an atmosphere of purified air may be got down to 0.06×10^{-6}.[4]

A very large number of methods of preparing conductivity water have been proposed.[5] The writer finds that water as good as that furnished by most of the elaborate stills is obtained by simple distillation, from a glass retort, of good distilled water to which a little potassium permanganate has been added, and condensing in a Jena glass tube fitted inside a Liebig's condenser, the corks being covered with tinfoil The first distillate is rejected till a test with a conductivity cell gives not more than $1 - 2 \times 10^{-6}$ ohm^{-1}. The most convenient laboratory still for conductivity water he has found to be the pan still of Bousfield.[6]

The water is kept in steamed-out glass bottles or porcelain vessels,[7] bottles coated inside with melted paraffin wax have been recommended. The temperature coefficient of conductivity water is about 2 per cent per 1° C.

The Water Correction: The correction of the measured value of the conductivity for the conductivity of the water has already been mentioned The water correction has been discussed by Kendall,[1] who concluded that if chemically pure water were available no correction would be required. Washburn[2] does not agree; even with water of conductivity 0.04×10^{-6} the correction is 0.3 per cent at 0.0001 *n*. and that at 0.00001 *n*. is 3 per cent. With 0.06×10^{-6} water the corrections are not much larger. The advantage of ultrapure water is not the elimination of the water correction but elimination of uncertainty as to the appropriate method of applying the correction.

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[1] Leeds and Northrup Catalog No 48 (1919), p 5

[2] Kohlrausch, *Ann. Physik Erganzungsbd* 8, 1 (1878), Kohlrausch and Heydweiller, *Ann. Physik*, **53**, 209 (1894), Kohlrausch, *Z physik Chem*, **42**, 193 (1902).

[3] Nernst informed the writer that he had made unsuccessful attempts.

[4] Washburn, *J. Am Chem. Soc*, **40**, 109 (1918).

[5] Summary in Kendall, *J Am Chem Soc*, **38**, 2160 (1916), Jones and Mackay, *Z. physik. Chem.*, **22**, 237 (1897), Hantzsch and Barth, *Ber*, **35**, 210 (1902), Hulett, *Z physik.*
Chem., **21**, 297 (1896), Lorenz, *ibid*, **82**, 612 (1913), MacGregory, *Ann. Physik*, **51**, 126
(1894); Nernst, *Z. physik. Chem.*, **8**, 110 (1891), Ostwald, *Ann. Physik*, **40**, 735 (1890);
Paul, *Z. Elektrochem.*, **20**, 179 (1914), Pfeiffer, *Ann Physik*, **31**, 831 (1887), Schick, *Z.*
physik. Chem., **42**, 157 (1903); Kraus and Dexter, *J Am. Chem Soc*, **44**, 2468 (1922); Hart-
ley, Campbell and Poole, *J. Chem. Soc*, **93**, 428 (1908), Thole, *ibid*, **101**, 207 (1912); Bour-
dillon, *ibid.*, **103**, 791 (1913), Clevenger, *J. Ind Eng Chem*, **11**, 964 (1919), Kendall, *J.*
Chem. Soc, **101**, 1275 (1912).

[6] *J. Chem. Soc.*, **87**, 740 (1905), **101**, 1113 (1912), as supplied, the tin tube is sometimes soldered and useless.

[7] Kohlrausch, Leitvermögen, 115 ff.

When very pure water stands exposed to air it dissolves carbon dioxide and its conductivity rises, at first rapidly, then more slowly, until a maximum is reached at about 0.8 to 1.0×10^{-6}, when the water is in equilibrium with the carbon dioxide in the atmosphere.[3] This may be called "equilibrium water." If solutions are to be exposed to the air, such water is better than the purest water as far as constancy of conductivity is concerned, but equilibrium water is just as difficult to maintain at a constant conductivity as the purest water.[4]

Washburn has described methods of correcting for the dissolved carbon dioxide and for salts, but he emphasizes[5] that some uncertainty attaches to the correction on account of: (i) the magnitude of the correction; (ii) the proportion of conductivity due to CO_2; (iii) the nature of the products of hydrolysis and other impurities than CO_2; (iv) difficulty of keeping the water constant in composition. He points out that his results are not in agreement with those of Arrhenius,[6] who found that the carbonic acid correction for the salt of a strong acid and base (sodium chloride) dissolved in equilibrium water at 18° is negative in sign, starting at zero for high dilutions, reaching a largest value of -0.1 per cent at 0.0001 *n*., and then falling away to zero at higher concentrations, whereas Washburn's correction is positive in sign and should increase continuously with dilution, reaching a maximum value of only $+0.016$ per cent at high dilutions. This refers to carbonic acid as the only impurity and the equation is:

$$P_m = 1.15 \times 10^5 \alpha k_w / \Lambda_{H_2CO_3} K_e,$$

where P_m = percentage correction to be added to the conductivity (specific) after the usual water correction has been applied, viz., to κ (solution) $- \kappa_0$ (water); k_w = specific conductance of the water; $K_e = \alpha^2 c/(1-\alpha)$ for the salt; $\Lambda_{H_2CO_3}$ = equivalent conductivity of H_2CO_3. E.g., with 0.00005 *n*. KCl, $K_e = 0.0210$; $\alpha = 1$; $\Lambda_{H_2CO_3} = 353$; hence if $k_w = 1 \times 10^{-6}$, $P_m = 0.016$ per cent.

If saline impurities are present also, the correction is larger, and Washburn proposes a total correction of Kohlrausch's data of $+0.02$ per cent at 0.0001 *n*.

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[1] *J. Am. Chem. Soc.*, **38**, 1480, 2460 (1916); **39**, 7 (1917).

[2] *J. Am. Chem. Soc.*, **40**, 109 (1918).

[3] Kohlrausch, *Ges. Abh.*, **2**, 871; Kendall, *J. Am. Chem. Soc.*, **38**, 1480, 2464 (1916).

[4] Kohlrausch, *loc. cit.*, p. 996.

[5] *J. Am. Chem. Soc.*, **40**, 109 (1918).

[6] *Medd. K. Vetensk. Akad. Nobelinst.*, no. 42, **2**, p. 10 (1913); Kendall, *J. Am. Chem. Soc.*, **39**, 15 (1917).

and 0.0002 *n*.; of + 0.01 per cent for 0.0005 *n*., and 0.001 *n* , and no correction for higher concentrations. The corrections for salts of weak acids and bases, and for salts of higher valence types, are regarded as problematical.

Errors in Conductance Measurements: The influence of temperature on conductance amounts to about 2 per cent per 1° C., so that, to obtain an accuracy of 0.1 per cent, temperature control to 0.05° is necessary, i.e., a thermostat must be used. The Lowry bulb regulator filled with toluene, with an electrical mercury contact operating a relay and heating lamp, with good stirring, gives excellent results, especially if the capillary stem is prolonged inside the wider top by a capillary tube fitted in with a little cement, inside which capillary tube fits the platinum wire cut-out. The thermometer is placed alongside the cell and ample time allowed to attain temperature equilibrium. The current from the coil heats the liquid, and it should not be kept running for long. The best way to reduce the current from the coil is to insert resistance in the primary circuit as long as the hammer break still works, otherwise a very large resistance is necessary in the secondary circuit, from one pole of the coil; but, this may cause trouble by static charging of the telephone unless the other pole of the coil is earthed.

The resistance of the leads from the cell to the bridge may be found with mercury in the cell, and should be subtracted from all measurements.[1]

With an alternating current of sufficiently high frequency, and the electrodes well platinized, polarization is practically eliminated. Elimination of polarization is effected[2] by (*a*) platinizing and increase of frequency; (*b*) compensation and increase of frequency. It can always be eliminated by the usual process of platinizing even when comparatively low frequencies (not greater than 1000) are used. The decomposing action of platinum black on the solution may, however, set a limit to this method, in which case, if the solution is not too concentrated, polarization may be eliminated by simply increasing the frequency. Taylor and Acree[3] extrapolate from frequencies of 500, 750, 1000 and 1500, obtained by the Vreeland Oscillator, to infinite frequency. They also use the formula

$$(R_f - R_\infty)/L_f f = \text{const} ,$$

where *R* and *L* are resistance and inductance, *f* is the frequency; and they also show that capacity does not depend on a gas layer on the electrodes. A conductivity cell acts as a resistance in series with a simple condenser with a leak. Eastman[4] considers that the conductivity is smaller at zero frequency than in the range immediately above zero His measurements show a difference of only 0.02 to 0.03 per cent with direct current and with 1000 cycles alternating, but he considers this difference is in the right direction Haworth[5] considers that extrapolation to infinite frequency gives the right resistance. The resistance is independent of frequency if the potential measuring electrodes are not in the main current stream.

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[1] Washburn, *J. Am. Chem Soc* , **39**, 235 (1917), recommends enclosing the leads, kept straight and parallel, in an earthed metal sheath.

[2] Nernst, *Z. physik. Chem* , **14**, 622 (1894). Déguisne, *Diss* , Strasburg (1895), Washburn, *J. Am. Chem. Soc.*, **38**, 2456 (1916).

[3] *J. Am. Chem. Soc.*, **38**, 2415 (1916).

[4] *J. Am. Chem. Soc.*, **42**, 1649 (1920).

[5] *Trans. Farad. Soc.*, **16**, 365 (1920).

The effect of polarization is not merely to reduce the sharpness of the minimum but also to shift the center of this;[1] its effect is not simply a pure condenser reactance, but an increase of effective resistance accompanies it, which is smaller with large electrodes[2] and higher frequency. This is attributed to dissipation of energy owing to the incompletely reversible electrode reaction. Washburn[3] suggests that this points to some catalytic activity of the platinum black. Curtis and Taylor[4] tested Wien's method of electrically compensating for condenser reactance by inserting a variable pure inductance, and find that it gives results within 0.02 per cent of those with platinized electrodes.

Self-inductance (mainly of the bridge coils) and electrostatic capacity in the bridge arms may arise with alternating currents, and it would be difficult to estimate and allow for them. Fortunately, when they are present, there is a want of sharpness in the telephone minimum, and as long as good readings are obtained it may be assumed that inductance, capacity and polarization are negligible, unless the resistances to be measured are very large or very small. The effect of the three sources of error are summarized in the following table:[5]

	Self Induction large when	Polarization large when	Capacity large when
Frequency is	great	small	great
Resistance is	small	small	great

The frequency in the circuit is much higher than that of the hammerbreak of the coil.[6]

Capacity is appreciable in bifilar wound coils, and these should not be used of resistance greater than 500 ohms; higher units should have Chaperon winding. The effect of capacity is appreciable when a liquid of high resistance is in the cell; it is also present owing to the water in the thermostat acting as a conducting coating of a Leyden jar. This may be got over by immersing the cell in a vessel of paraffin oil.[7] A small condenser, e g., of tinfoil on glass, sliding between similar plates, or tinfoil between paraffined paper, may also be inserted in parallel with the bridge arm opposite the one in which capacity occurs and varied till the minimum is sharp. A condenser in series with a circuit can nullify inductance when $f = 1/2\pi\sqrt{LC}$; f = frequency, L = inductance, C = capacity. If corresponding inductance and capacity are present, the circuit behaves as a non-inductive one[1]

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[1] Wien, *Ann. Physik*, **47**, 626 (1892).

[2] Wien, *Ann. Physik*, **58**, 37 (1896); Neumann, *ibid.*, **67**, 499 (1899). Haworth, *loc. cit.*, has overlooked this.

[3] *J. Am. Chem. Soc.*, **38**, 2459 (1916).

[4] *Phys. Rev.*, **6**, 61 (1915); Wolcott, *Ann. Physik*, **12**, 653 (1903).

[5] Lehfeldt, Electrochemistry, London (1908), p. 57; Kohlrausch, Leitvermogen, p. 55 f.; Washburn, *J. Am. Chem. Soc.*, **38**, 2431 (1916); Kruger, *Z. physik. Chem.*, **45**, 1 (1903); Oberbeck, *Ann. Physik*, **19**, 625 (1883); **21**, 139 (1884); Schlesinger and Read, *J. Am. Chem. Soc.*, **41**, 1727 (1919); Wien, *Ann. Physik*, **58**, 37 (1896); **59**, 267 (1896).

[6] Lenard, *Ann. Physik*, **39**, 619 (1890).

[7] Kohlrausch, *Ann. Physik*, **49**, 225 (1893); Leitvermögen, p. 59.

Equivalent Conductance at Infinite Dilution: The value of Λ increases with dilution and approaches a limiting value which is reached at different dilutions for different types of electrolytes and is known as the limiting value of the equivalent conductance for infinite dilution, Λ_∞, or zero concentration, Λ_0. In the light of the electrolytic dissociation theory the interpretation of Λ_∞ is clear: it refers to complete ionization. The kind of increase of Λ with dilution is shown in the following table (Kohlrausch):

TABLE I

Λ_φ AT 18° C.

Dilution φ in cc.	KCl	$\frac{1}{2}CuSO_4$	CH_3COOH
10^3	98.3	25.8	1.32
10^4 .	112.0	43.9	4.60
10^5	122.4	71.7	14.3
10^6 ..	127.3	98.5	41.0
10^7... .. .	129.1	110.0	107.0

It is evident that, in the case of KCl, the limiting value can be calculated with some accuracy by extrapolation; in the case of $\frac{1}{2}CuSO_4$ the approach to a limiting value is apparent, but this cannot be calculated by extrapolation from the figures given; in the case of acetic acid it is evident that, even at high dilutions, the limiting value is far from being attained. In the case of weak electrolytes, such as acetic acid, the limiting value can be found by indirect methods only, as explained later.

For the purposes of interpolation and extrapolation the values of Λ at different concentrations are plotted against the cube root or the logarithm of the concentration. The first method is used by Kohlrausch,[2] and the curves in Figs. 9 *a* and *b* show the results with some typical electrolytes and the character of the extrapolation may be seen. For very dilute solutions Λ may be plotted against the square root of the concentration in equivalents per *liter*. The objection to Kohlrausch's method that it assumes a certain relation between Λ and the concentration which may not hold at very high dilutions has little weight except in cases of extreme accuracy.

The Λ curves of acids and bases are more difficult to extrapolate than those of salts, on account of the greater influence of impurities (CO_2, NH_3) in the

[1] Taylor and Acree, *J. Am. Chem. Soc.*, **38**, 2403 (1916), find agreement to 0.001 per cent with (*a*) inductance, (*b*) condenser, used to balance the capacity of the conductivity cell. Technical methods of measuring conductivity: Keeler, *Trans. Am. Electrochem. Soc.*, **38**, 113 (1920).

[2] *Ann. Physik*, **26**, 161 (1885), **50**, 385 (1893), Liebenow, *Z. Elektrochem.*, **8**, 933 (1901), Kohlrausch and Maltby, *Wiss. Abhandl. P. T. Reichsanstalt*, **3**, 157 (1900)

water, at high dilutions. The curves then exhibit maximum values of Λ at high dilutions, and then fall off rapidly.[1]

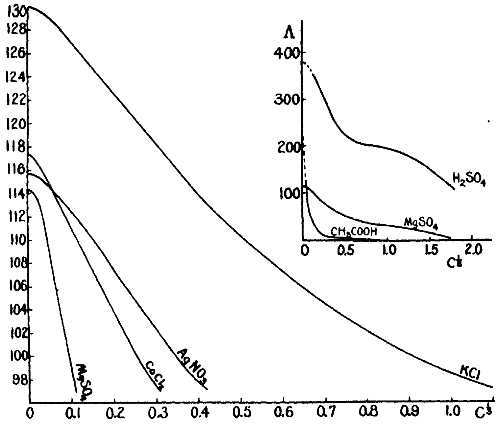

FIG. 9a. Λ – $C^{1/3}$ Curves

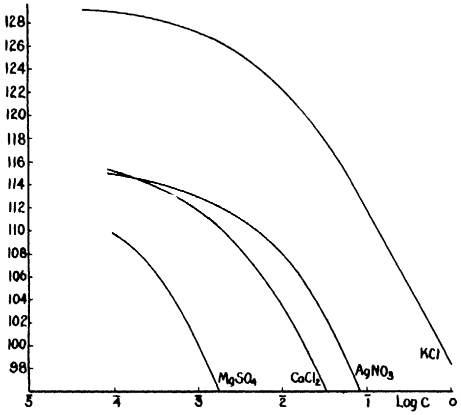

FIG. 9b. Λ – Log C Curves

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[1] Whetham and Paine, *Proc. Roy. Soc.*, **81**, 58 (1908); Whetham, *Phil. Trans.*, **194**, 353 (1900); Kendall, *J. Am. Chem. Soc.*, **39**, 12 (1917); Washburn, *ibid.*, **40**, 122 (1918); Chittock, *Proc. Camb. Phil. Soc.*, **15**, 55 (1909). Some solutions exhibit a maximum specific conductance at a certain concentration; this is due to the interplay of ionization and concentration: sulphuric acid at 30 per cent (Kohlrausch and Holborn, Leitvermögen, p. 75); hydrochloric acid 18 per cent (Gibson, *Trans. Roy. Soc. Edinb.*, **48**, 117 (1912)); magnesium sulphate (Kohlrausch and Holborn, *loc. cit.*, p. 76).

Ostwald's Rule: An empirical relation discovered by Ostwald[1] states that $\mu_{1024} - \mu_{32} = 10 . y_+ . y_-$, where μ_{1024} and μ_{32} are molar conductances at dilutions of 1024 and 32 *liters*, respectively, of salts of strong acids or bases, and y_+ and y_- the valencies of the kation and anion. The rule holds very approximately to $y = 6$ and is often useful in finding the basicity of acids or bases ($y_+ = 1$ and $y_- = 1$, respectively).[2]

On the basis of this rule, Bredig (*loc. cit.*) compiled the following table, giving the values to be added to the molar conductance of a salt at 25° at the given dilution to make up μ_∞. The accuracy is usually about one unit, and the table is useful for approximate work. The first column gives $y_+ . y_-$. E.g., for KCl, this is 1 × 1; for $BaCl_2$, 2 × 1; for $Al_2(SO_4)_3$, it is (3 × 2 = 6). Bracketed values are less certain. (Conductances are in ohm^{-1}, not Siemens' units.)

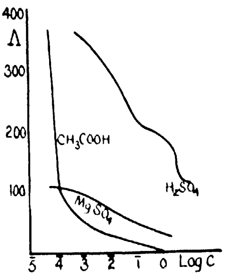

Fig. 96. Λ–Log C Curves

TABLE II

Conductance Calculations for Infinite Dilution

	Dilution (liters per mol.)					
$y_+ . y_-$	32	64	128	256	512	1024
1.	15	11.7	8.5	6.4	4.2	3.2
2	(26.6)	22.3	17	12.7	8.5	6.4
3	(39.3)	31.8	24.4	18	12.7	8.5
4	(55)	44.6	33	24.4	17	10.6
5	(66)	56.3	41.5	30.8	22.3	13.8
6.	(75.5)	(63.8)	51	38.3	26.6	17

This table, of course, can be used only for approximation;[3] the values calculated from the higher dilutions are often higher than those found from the lower dilutions.

Calculation of Λ_∞: The extrapolation of Λ to infinite dilution is a matter of importance when the question of the validity of the law of mass action at high dilutions is considered. Kohlrausch, as mentioned, extrapolated by plotting Λ against $c^{1/3}$, assuming[4]

$$\Lambda = \Lambda_0 - ac^{1/3} \qquad \text{or} \qquad \Lambda = \Lambda_\infty - a\varphi^{-1/3}.$$

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[1] *Z. physik. Chem.*, **1**, 74 (1887), **2**, 840 (1888); Walden, *ibid.*, **1**, 529 (1887), **2**, 49 (1888); Bredig, *ibid.*, **13**, 191 (1894).

[2] On methods of making up to these dilutions see Klemenc, *Chem. Z.*, **35**, 1420 (1911).

[3] Lorenz, *Z. anorg. Chem.*, **108**, 81 (1919), Lorenz and Posen, *ibid.*, **96**, 90 (1916); Wegscheider, *Z. Elektrochem.*, **18**, 277 (1912).

[4] Leitvermögen, p. 107.

The value of a varies from one salt to another, but it has, at 18°, approximately the value 400 for uni-univalent electrolytes. An accuracy of only 1 per cent is claimed[1] At the highest dilutions a better approximation is given, according to Kohlrausch,[2] by the equation

$$\Lambda = \Lambda_0 - bc^{1/2}$$

(for c from 0.002 or 0.005 to 0 equiv. per liter).

Lorenz[3] gives values of a and b for basic organic kations (110 substances) for which both formulae apply equally well: $\mu_\infty - \mu = 91.54c^{1/2}$; $\mu_\infty - \mu = 58.2c^{1/3}$. The equation with $c^{1/2}$ is said by Kohlrausch to be "surprisingly exact." For higher concentrations (to 0.1 n.) he proposes[4]

$$\Lambda_0 - \Lambda = B\Lambda^p c^{1/2},$$

with another constant p, varying from substance to substance. This does not hold for bi-bivalent electrolytes.

For concentrated solutions Gibson[5] proposes

$$\Lambda' = \Lambda_0 - Dc',$$

where

$$\Lambda' = \kappa/c',$$

c' being the concentration in equivalents per *gram of solution*. This does not hold for dilute solutions, and cannot be used for extrapolation to Λ_0.

Randall[6] finds that if the percentage ionizations of salts are plotted against $c^{1/2}$ the curves fall into non-intersecting groups according to the valence types of the salts. Salts of the same valence type also divide themselves into distinct groups, e.g., halides of alkali metals and ammonium,[7] and, in this case, the degrees of ionization, α, become more nearly equal as zero concentration is approached. If α, Λ, and Λ_0 are known for one salt of a group, α may be assumed the same at a given concentration for another member, and thus, if Λ is known, Λ_0 may be calculated from $\alpha = \Lambda/\Lambda_0$. The values of Λ_0 so found for different concentrations are then plotted against $c^{1/2}$ and extrapolated to zero concentration to give a final value of Λ_0. A method similar to that of Kohlrausch was used by A. A. Noyes and his collaborators.[8] All such methods imply, however, that the law of mass action is not obeyed even at extreme dilutions.[1] W. R. Bousfield[2] has used the equation

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[1] The same equation was put forward by A. W. Porter, *Trans. Farad. Soc.*, **15**, 122 (1919); it holds very approximately for $ZnCl_2$ and Na_2SO_4 as well as for LiCl.

[2] *Loc. cit.*, p. 108, the equation $\Lambda = \Lambda_0 - ac^{1/3}$ was first used by Kohlrausch, *Ann. Physik*, **26**, 161 (1885), *ibid.*, **50**, 385 (1893), Barmwater, *Z. physik. Chem.*, **28**, 115 (1899); cf. Storch, *ibid.*, **19**, 13 (1896), Bancroft, *ibid.*, **31**, 188 (1899), Kohlrausch, *Sitzber. Preuss. Akad. Wiss.*, ii, 1002 (1900), Kohlrausch and Steinwehr, *ibid.*, i, 581 (1902), Kohlrausch, *Z. Elektrochem.*, **13**, 333 (1907).

[3] *Z. anorg. Chem.*, **108**, 81, 191 (1919).

[4] Leitvermogen, p. 108, Lorenz, *Z. anorg. Chem.*, **108**, 81, 191 (1919).

[5] *Trans. Roy. Soc. Edinb.*, **45**, 241 (1906).

[6] *J. Am. Chem. Soc.*, **38**, 788 (1916).

[7] This was well known to Kohlrausch, Leitvermogen, p. 108.

[8] Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 462 (1912).

$$\alpha^{3/2}/(1-\alpha) = Kh^{1/2},$$

where

$$\alpha = \Lambda\eta/\Lambda_\infty\eta_\infty,$$

η being the viscosity, and h the number of mols. of water per mol. of salt, for solutions of KCl. He also proposes

$$\alpha/(1-\alpha) = h^{1/2}.10^{1-\alpha}/5.37$$

for the same solutions, which gives very exact results from 0.0001 *n.* to 0.1 *n.* In a further paper[3] he proposes another equation. These give very exact interpolations, but their use in the extrapolation to Λ_∞ is doubtful, for the reason just given. Partington[4] suggested that the law of mass action holds, even for strong electrolytes, at very high dilutions, and proposed the formula:

$$\alpha^2c/(1-\alpha) = K + kc\alpha,$$

or

$$\Lambda^2c/\Lambda_0(\Lambda_0-\Lambda) = K + kc(\Lambda/\Lambda_0),$$

which reduces to the mass action equation

$$\alpha^2c/(1-\alpha) = K$$

when c tends to zero. Although this is not adequate to deal with strong electrolytes,[5] the idea that the law of mass action is obeyed at high dilution seems to have been established by the experiments of Washburn and collaborators.[6] In 1912 MacDougall[7] and Kraus and Bray[8] proposed a modification of this formula, viz.,

$$\Lambda^2c/\Lambda_0(\Lambda_0-\Lambda) = K + k(c.\Lambda/\Lambda_0)^h,$$

where h is another constant. The value of Λ has been "corrected" for viscosity, i.e., the experimental value has been multiplied by η/η_0. This equation holds very satisfactorily for aqueous and non-aqueous solutions, but in the application to aqueous solutions Kraus and Bray found it necessary to alter fundamental data, e.g., the value of Λ_0 for KCl found by Kohlrausch and Maltby[9] from 129.9 to 128.3, in a manner which even at the time could not be regarded as admissible. The value 128.3 had actually been exceeded by Kohlrausch and

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[1] Cf. Bates, *J. Am. Chem. Soc.*, **35**, 522 (1913). Wegscheider, *Z. physik. Chem.*, **69**, 603 (1909).

[2] *Phil. Trans.*, A, **206**, 155 (1906). *J. Chem. Soc.*, **103**, 307 (1913).

[3] *J. Chem. Soc.*, **105**, 1809 (1914).

[4] *J. Chem. Soc.*, **97**, 1158 (1910).

[5] Partington, *Trans. Farad. Soc.*, **15**, 104 (1919).

[6] *J. Am. Chem. Soc.*, **40**, 131 (1918).

[7] *J. Am. Chem. Soc.*, **34**, 855 (1912).

[8] Science, **35**, 433 (1912); *ibid.*, *J. Am. Chem. Soc.*, **35**, 1414 (1913), **37**, 1315 (1915).

[9] *Wiss. Abh. d. P. T. Reichsanstalt*, **3**, 156 (1900).

Maltby in their measurements at low concentrations, and the force of this criticism of Kraus and Bray's treatment of experimental data of high accuracy, made by the writer[1] and by Washburn,[2] is now admitted by Kraus.[3] Bates[4] found that the experiments of Kohlrausch and Maltby could be completely represented, with an accuracy even greater than that obtained by Kraus and Bray, to the highest concentrations, by the empirical formula:

$$\log \Lambda^2 c/\Lambda_0(\Lambda_0 - \Lambda) = \log K + k(c.\Lambda/\Lambda_0)^h,$$

where K, k, h have, of course, different values from those in Kraus and Bray's equation. The theoretical meaning of this may not be very clear, but it serves to show that agreement or non-agreement with empirical equations is not a very safe guide in the criticism of experimental data. Washburn[5] points out that K is not necessarily the true value of the mass action constant for $c = 0$. He used a graphical method of extrapolation, depending on two assumptions: (i) Lim $dK/dc = 0$ when $c = 0$, and (ii) the curve connecting K and c does not show deviations from the law of mass action which increase with dilution. The values of K are plotted against c for various assumed values of Λ_0, and of the latter those are rejected which cause the curves at high dilutions to assume radical changes in direction (see Fig. 10). In this way, it is claimed, the value of Λ_0 may be found with an accuracy of 0.01 per cent, provided the conductance data are equally accurate and extend down to 0.00002 n. If the conductance data extend only to 0.0001 n., the value of Λ_0 is accurate to about 0.2 per cent.

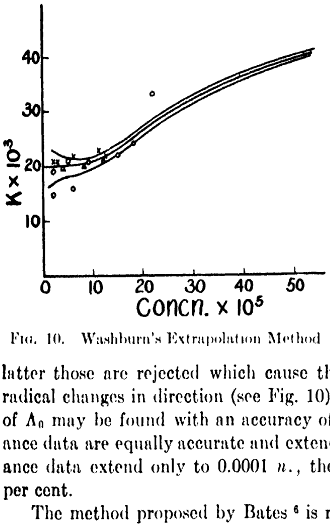

Fig. 10. Washburn's Extrapolation Method

The method proposed by Bates[6] is really the same in an analytical form. The equation of Storch:

$$\Lambda^n c^{n-1}/\Lambda_0^{n-1}(\Lambda_0 - \Lambda) = \text{const.}$$

is applied by fitting it to a small piece of the curve at a time, the two parameters Λ_0 and n being allowed to vary at different parts of the curve. A lower limit of Λ_0 is found by putting $n = 2$ (law of mass action) and finding Λ_0 from the two lowest concentrations. An upper limit of Λ_0 is found by trial, taking the largest value of Λ_0 which does not cause corresponding values of n to pass through a maximum. Bates's values for Λ_0 are about 0.05 unit lower than Washburn's—an altogether inappreciable amount.

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[1] *Trans. Farad. Soc.*, **15**, 98 (1919).

[2] *J. Am. Chem. Soc.*, **40**, 122 (1918).

[3] *J. Am. Chem. Soc.*, **42**, 1, 1087 (1920).

[4] *J. Am. Chem. Soc*, **37**, 1431 (1915).

[5] *J. Am. Chem. Soc.*, **40**, 122 (1918); cf. Kendall, *ibid.*, **40**, 622 (1918).

[6] *J. Am. Chem. Soc.*, **35**, 519 (1913).

The method of extrapolation used by Washburn has been criticized by Kendall[1] and by Kraus.[2] Kendall points out that the method is the same as one used by himself[3] in 1912, but Washburn, whilst giving Kendall credit for using the method in a particular case, claims that his own method is more general, and Kendall has admitted the claim.[4] Kraus's paper is mainly concerned with the manner in which K varies with c. He rejects his former incorrect assumption of the inaccuracy of Kohlrausch and Maltby's data, but now applies his equation beginning at a concentration of 0.02 *n*. instead of 3 *n*., as previously, and finds, with quite different new values of the *four* parameters in it, that the dilute end of the curve, which he formerly rejected *in toto* as inaccurate, can now be very satisfactorily fitted, "not unnaturally," as Washburn (*loc. cit.*) remarks. The value of K found is very different from Washburn's, viz., 10×10^{-4} instead of 200×10^{-4} (Washburn).

Kraus now[5] appears to think that his value of K is too small. Kraus's objection that the plots of the first and second derivatives of Weiland's K, c curve, on which Washburn's calculations are based, are irregular, seems to the writer to have very little weight, since small errors would then be greatly magnified. His objection to Washburn's method of extrapolation, on the other hand, seems quite sound, although Washburn does not seem disposed to admit it, and some further theoretical support for the method should be given apart from the assumption of the ultimate obedience to the law of mass action at high dilutions. The region of concentrations employed by Weiland extends, however, so close to infinite dilution, that Washburn's values are probably very nearly correct. Kraus's disposition to treat Weiland's data as possibly inaccurate is rightly characterized by Washburn[6] as too nearly resembling his former treatment of Kohlrausch and Maltby's figures to merit very serious consideration.

Lorenz and Landé[7] assume complete ionization at all dilutions and consider that changes of conductivity are due to changes in the mobility of the ions on dilution. Instead of the expression

$$\Lambda = \alpha(u_0 + v_0)$$

they take

$$\Lambda = u + v \qquad \text{and} \qquad \Lambda_0 = u_0 + v_0.$$

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[1] *J. Am. Chem. Soc.*, **40**, 622 (1918).

[2] *J. Am. Chem. Soc.*, **42**, 1, 1087 (1920).

[3] *J. Am. Chem. Soc.*, **101**, 1275 (1912).

[4] *J. Am. Chem. Soc.*, **42**, 1077 (1920).

[5] Properties of Electrically Conducting Systems, 1922, p. 100.

[6] *J. Am. Chem. Soc.*, **42**, 1090 (1920).

[7] *Z. anorg. Chem.*, **125**, 59 (1922).

The changes of mobility with dilution

$$u/u_0 = x \qquad \text{and} \qquad v/v_0 = y$$

are assumed to be characteristic for each ion. However,

$$(1 - x_{K^\cdot})/(1 - y_{Cl'}) = \text{const.} = a,$$

$$(1 - x_{Na^\cdot})/(1 - y_{Cl'}) = \text{const.} = b,$$

and

$$(1 - x_{Na^\cdot})/(1 - x_{K^\cdot}) = \text{const.} = c,$$

where $a = 1.079$, $b = 1.396$, and $c = 1.292$. These values are easily found for salts. In the case of acids and bases the sodium or potassium salt or the chloride is used. Thus, in the case of the anion, the conductivity of the potassium salt is found at two concentrations:

$$c_1\Lambda_1 = u_{K_1^\cdot} + v_1 \qquad \text{and} \qquad c_2\Lambda_2 = u_{K_2^\cdot} + v_2.$$

If $y = v/v_0$, then

$$(1 - x_1)/(1 - y_1) = (1 - x_2)/(1 - y_2) = \text{const.},$$

whence v_0 can be found.

Another method[1] is based on Herz's theory (see later). Values of Λ are plotted against $c^{1/3}$ on a prescribed scale, and the curve transformed to a form of the universal curve

$$\Lambda_0 - \Lambda = f(c^{1/3}).$$

By comparing this with a series of standard curves on transparent paper on the same scale the value of Λ_0 can be read off. Lorenz[2] from a review of available data concludes that it is not possible to say which of Kohlrausch's equations,

$$\Lambda_0 - \Lambda = ac^{1/2} \qquad \text{and} \qquad \Lambda_0 - \Lambda = bc^{1/3},$$

is more accurate. Since the deviations from the mean values show no relation to the constitution of the ions, the constants a and b are "universal," and he calculates $a = 91.54$ and $b = 58.2$ for organic ammonium bases. The two equations give slightly different values of Λ_0, and the formula

$$\Lambda_0 - \Lambda = ac^n$$

is proposed.

The theoretical consideration of the deviations from the law of mass action, which lie at the root of all methods of extrapolation to Λ_0, will be considered in a later section.

Conductance and Viscosity: The resistance offered to the motion of the ions in a solution has an effect on the conductivity, and the viscosity of the solution may thus be expected to have some influence on conductance. This will be small below concentrations of about 0.1 *n*., since such solutions usually have practically the same viscosity as pure water, but at higher concentrations the calculated ionization may be changed by 7 or 8 per cent according as viscosity is or is not taken into account. The effect of viscosity seems first to have been pointed out by G. Wiedemann in 1856.[1]

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[1] Lorenz, *Z. anorg. Chem.*, **118**, 209 (1921).

[2] *Z. anorg. Chem.*, **108**, 81 (1919).

At infinite dilution the separate ions should move independently, and it would be expected that the motion of the ions would then depend only on their nature and on the solvent. This does not appear to be the case;[2] the product $\Lambda_\infty \eta$ (η = viscosity) varies from solvent to solvent, so that the equivalent conductance in one solvent cannot be calculated accurately from that in another by multiplication by the inverse ratio of the viscosities. If the conductivities of the individual ions are compared, the ratio varies from ion to ion, so that the ratios of Λ_∞ for the same solute in different solvents cannot be constant.

At moderately high concentrations the viscosity usually increases with the concentration, but sometimes in aqueous solutions it passes through a minimum. It depends both on solute and solvent. If the speeds of the ions depend on the viscosity, they will also depend on concentration, so that the equation of Kohlrausch-Arrhenius $\alpha = \Lambda/\Lambda_\infty$, will no longer be true.

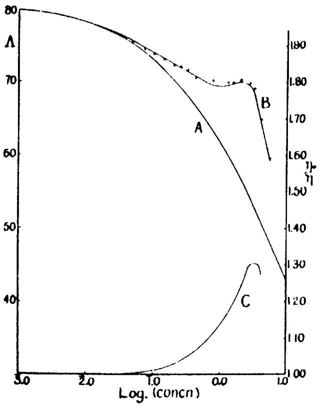

FIG. 11. Influence of viscosity change on conductivity of aqueous KCl soln. at 0°. A is the uncorrected curve. B is the curve plotted from the equation $(c\Lambda')^2/c\Lambda_0(\Lambda_0 - \Lambda') = \text{const.}\ (c\Lambda'/\Lambda_0)^{n-1}$, where const. = 2.62, Λ_0 = 81.12, n = 1.51 and $\Lambda' = \Lambda\eta/\eta_0$. C is the fluidity curve at 0°, i.e., the plot of η_0/η against log (concn.).

The work of Arrhenius[3] and of Ludeking[4] seems to show that the ionic and bulk viscosities are not identical, because a jelly containing salt conducts almost as well after as before solidification. The assumption of inverse proportionality between conductance and viscosity has often been made, i.e., it is supposed that $(\Lambda/\Lambda_0)(\eta/\eta_0)$ gives a better value for α than the simple ratio Λ/Λ_0.[5] It has been definitely shown, however, that the simple proportionality between conductance and fluidity (1/viscosity) as-

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[1] *Ann. Physik*, **99**, 228 (1856).

[2] Kraus and Bray, *J. Am. Chem. Soc.*, **35**, 1383 (1913).

[3] *Brit. Ass. Rep.*, p. 344 (1886).

[4] *Ann. Physik*, **37**, 172 (1889).

[5] Bousfield and Lowry, *Phil. Trans.*, **204**, 289, 291 (1904); Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 454 (1912).

sumed does not exist.[1] Johnson[2] considers that, except in the cases of $H^{\cdot}$ and OH' *ions, the equivalent conductance of each ion is a function of fluidity,* $\phi = 1/\eta$, *of the form* $\Lambda = k\phi^m$, where m is a constant varying from 0.81 to 1.03 *for various ions. This would lead to the expression:*[3]

$$\alpha = \frac{\Lambda}{\Lambda_0}\left(\frac{\eta}{\eta_0}\right)^m = \frac{\Lambda}{\Lambda_0}\left(\frac{\phi_0}{\phi}\right)^m$$

for the ionization, η_0 being the viscosity of the pure solvent. The value of m is usually less than 1, but approaches 1 for slowly moving ions. The relation does not apply to acids and bases, for which the equation: $\alpha = \Lambda/\Lambda_\infty'$, is proposed,[4] in which Λ is the equivalent conductance of a solution above which the vapor pressure of water is p, and Λ_∞' is the value for infinite dilution when a non-electrolyte[5] is added so as to give the solution the same viscosity and vapor pressure as the first solution.

Change in viscosity may in general be brought about by: (i) change of concentration (including addition of a third substance), (ii) change of pressure, (iii) change of temperature. Kraus[6] has considered these factors separately in connection with ionic mobility. Solutions which exhibit a negative viscosity effect (i.e., viscosity *decreases* with concentration increase) have conductances directly proportional to the fluidity, and the same also probably holds for changes of viscosity due to change of external pressure. As a rule corrections cannot be made in this way with solutions exhibiting a positive viscosity effect (i.e., viscosity *increases* with concentration increase), although it may sometimes be applied by considering each ion separately. In the relation[4] $\Lambda/\Lambda' = \eta^m$, where Λ and Λ' are respectively the equivalent conductances in media of unit viscosity and viscosity η, the value of m approaches 1 with large ions and when the molecules of added non-electrolyte are small. This has been confirmed by Kieran[7] with solutions of HCl and KCl in presence of sucrose. It is considered that the change in the true transport number of an electrolyte with change of concentration is due to the different effects of viscosity on the two ions. In non-aqueous solutions, the ionic velocities change much less than the fluidities, although at high concentrations a marked influence is apparent. In such cases, correction of ionization for viscosity is not possible.

At higher temperatures, the velocities of the different ions in aqueous solutions tend to a common limit, which has been supposed to indicate that the ions become equal in size.[8] The equality in size has been assumed to indicate hydration, which would then increase with rise of temperature.[9]

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[1] Green, *J. Chem. Soc.*, **93**, 2023, 2049 (1908); Sidgwick and Wilson, *ibid.*, **99**, 1118 (1911).

[2] *J. Am. Chem. Soc.*, **31**, 1010 (1909).

[3] Washburn, *J. Am. Chem. Soc.*, **33**, 1461 (1911); Sachanov, *Z. Elektrochem.*, **19**, 588 (1913).

[4] Washburn and Williams, *J. Am. Chem. Soc.*, **35**, 750 (1913).

[5] The influence of non-electrolytes on ionization is discussed later.

[6] *J. Am. Chem. Soc.*, **36**, 35 (1914).

[7] *Trans. Farad. Soc.*, **18**, 119 (1922).

[8] Cf. Kohlrausch, *Ann. Physik*, **154**, 228 (1875); **62**, 209 (1897); *Sitz. ber. preuss. Akad.*, **26**, 572 (1902); Grotrian, *Ann. Physik*, **160**, 238 (1877); **8**, 259 (1879).

[9] Martin and Masson, *J. Chem. Soc.*, **79**, 707 (1901); Green, *ibid.*, **93**, 2023 (1908).

The viscosity varies with pressure,[1] and the pressure effect also varies with temperature. In the case of pure water the viscosity decreases rapidly with increase in pressure, the rapidity of decrease being less as the temperature rises. At very high pressures the effect changes sign, and the viscosity increases with pressure (inferred from the shape of the curves). With non-aqueous solvents, viscosity increases with pressure,[2] the increase being greater the greater the viscosity. With increase of concentration the decrease in viscosity with pressure in the case of aqueous solutions becomes smaller and ultimately becomes an increase. The effect of pressure increases when the temperature is lowered.[3]

Influence of Non-Electrolytes: The conductance of aqueous solutions usually diminishes on addition of non-electrolytes in not too large amounts, the influence being exerted partly on the ionization and partly on the mobilities of the ions.[4] With further addition the conductivity slowly increases.[5] The effect is closely related to the viscosity change,[6] although colloids have usually only a slight effect,[7] except in large amounts.[8] The temperature coefficient of such solutions is usually nearly the same as that of pure aqueous solutions, unless the viscosity is greatly affected.[9]

Influence of Pressure on Conductivity: The influence of pressure on conductivity has been very thoroughly studied. The equation:

$$(d\,lnK/dp)_T = \Delta V/RT$$

was deduced by Planck[10] for dilute solutions. K is the equilibrium constant

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[1] Cohen, *Ann. Physik*, **45**, 666 (1892).

[2] Cohen, *loc. cit.;* Rontgen, *Ann. Physik*, **22**, 510 (1884), Warburg and Sachs, *ibid.*, **22**, 518 (1884).

[3] Cohen, *loc. cit.*, Schmidt, *Z. physik. Chem.*, **75**, 305 (1910). On viscosity effects in very concentrated solutions see Rabinowitsch, *Z. physik. Chem.*, **99**, 338, 417, 434 (1921). On viscosity and conductance see H. C. Jones and his co-workers, *Am. Chem. J*, **37**, 405 (1907); **42**, 37 (1909); **46**, 131 (1911), *Z. physik Chem*, **61**, 641 (1908); **62**, 44 (1908); **81**, 68 (1912); **85**, 513 (1913); *J. Chim. Phys*, **12**, 385 (1914), *J. Am. Chem. Soc.*, **37**, 1194 (1915).

[4] Stephan, *Ann. Physik*, **17**, 673 (1882), Lenz, *M Acad. Petersb.*, **30**, No. 9 (1882); Arrhenius, *Z. physik. Chem.*, **9**, 487 (1892); Holland, *Ann Physik*, **50**, 201 (1893), Strindberg, *Z. physik. Chem.*, **14**, 161 (1894), Walden, *ibid*, **15**, 196 (1894), Cohen, *ibid*, **25**, 1 (1898); Walker and Hambly, *J. Chem. Soc.*, **71**, 61 (1897), Roth, *Z. physik. Chem*, **42**, 209 (1902), cf. Wildermann, *ibid.*, **46**, 43 (1903); Hartley, Thomas and Appleby, *J. Chem. Soc.*, **93**, 538 (1908); Green, *ibid.*, **93**, 2023, 2049 (1908).

[5] Arrhenius, *loc. cit.;* perhaps due to hydration of non-electrolyte.

[6] Stephan, Arrhenius, *loc. cit;* Massoulier, *Compt. rend*, **130**, 733 (1900); *supra*, Viscosity.

[7] Levi, *Gaz. chim. ital.*, **30**, 64 (1900).

[8] E. Wiedemann, *Ann. Physik*, **20**, 537 (1883), Tietzen-Hennig, *ibid.*, **35**, 407 (1888); Lüdeking, *ibid.*, **37**, 172 (1889).

[9] Di Ciommo, *Nuov. Cim*, **2**, 81 (1901), Starck, *Beibl. Ann. Physik*, **25**, 713 (1901). On conductivity of gelatine solutions see Palmer, Atchley and Loeb, *J. Gen. Physiol.*, **3**, 801 (1921).

[10] *Ann. Physik*, **32**, 494 (1887), Braun, *ibid*, **30**, 250 (1887), *Z. physik. Chem.*, **1**, 259 (1887); see under Thermodynamics.

and ΔV the change of volume in the dissociation of 1 mol. of electrolyte. From this, the change in conductivity may be calculated. The effect has been examined experimentally[1] and the theory generally confirmed.

Körber, who used pressures up to 3000 kgm./cm.^{2}, found an increase of conductivity, the magnitude of the effect depending on temperature. In the case of acetic acid at 20° C. the results agreed with Planck's formula, but at higher temperatures the conductivity increased instead of decreasing according to the formula. The effects of pressure on ionic friction and viscosity of the solvent correspond in the case of sodium chloride but not for the potassium salt. The influence of pressure on ionic friction is additive for the two ions in the case of strong electrolytes. With increase of temperature the isothermals representing the influence of pressure on ionic friction for different electrolytes tend to approach one another, but $H^{\cdot}$ ions are exceptional. Up to the highest pressures the direction of the influence of pressure on the conductivity of strong electrolytes is independent of concentration up to moderate concentrations, but the magnitude of the effect becomes smaller as the concentration increases. For dilutions greater than 1 mol. in 100 liters, the effect of the solvent water becomes appreciable.

Schmidt examined the effect in non-aqueous solutions, using eleven organic solvents. The effect was divided into three factors: (i) change of volume, (ii) change of ionization, (iii) change of viscosity. The latter is not included in Planck's formula. The relative importance of these was examined. The effect is much greater than in aqueous solutions in the case of strong electrolytes, but less in the case of weak electrolytes. The influence of pressure diminishes with rise of temperature and increase of concentration. In the case of NEt_4I the logarithm of the resistance increases proportionally to the pressure. With non-associating solvents the influence of pressure increases at 20° linearly with the viscosity of the solvent.

Drude and Nernst[2] pointed out that the experiments of Kohlrausch and Hallwachs[3] showed that the ionization of an electrolyte is always accompanied by a decrease in volume in the case of aqueous solutions, and they call this contraction of water in presence of free ions, *electrostriction*. It indicates that the dielectric constant of the solvent should be increased by pressure.[4] In aqueous solutions the contraction amounts to 10-12 cc. per equivalent of uni-univalent electrolyte ionized. In non-aqueous solutions[5] the corresponding figure is about 13 cc.

[1] Fink, *Ann. Physik*, **26**, 481 (1885); Fanjung, *Z. physik. Chem.*, **14**, 673 (1894); Piesch, *Ber. Wien Akad.*, **103**, 784 (1894); Lussana, *Nuov. Cim.*, **2**, 263 (1895); **5**, 357, 441 (1897); *Z. physik. Chem.*, **76**, 420 (1911); Tammann, *Z. physik. Chem.*, **17**, 725 (1895), Tammann and Bogojawlensky, *ibid.*, **27**, 457 (1898); Tammann, *Ann. Physik*, **69**, 767 (1899); Foussereau, *Compt. rend.*, **104**, 1161 (1887); Barus, *Am. J. Sci.*, **40**, 219 (1890); Körber, *Z. physik. Chem.*, **67**, 212 (1909); **77**, 420 (1911); Schmidt, *ibid*., **75**, 305 (1910); Luther in Winkelmann's Physik, IV, i, 433 ff., for other factors supposed to influence conductivity.

[2] *Z. physik. Chem.*, **15**, 79 (1894).

[3] *Ann. Physik*, **53**, 14 (1894); Kohlrausch, *ibid.*, **56**, 185 (1895).

[4] Non-electrolytes, see Polowzow, *Z. physik. Chem.*, **75**, 513 (1911).

[5] Carrara and Levi, *Gazetta*, **30**, ii, 197 (1900); Walden, *Z. physik. Chem.*, **60**, 87 (1907); Nernst, Lehrbuch, 8-11 Aufl., p. 449.

The relation

$$\Delta = \frac{\Lambda}{\Lambda_\infty}(A - B) + B,$$

where Δ is the percentage change in density per gram equivalent of dissolved electrolyte, and A, B are constants representing respectively the percentage changes in density caused by one gram equivalent of ionized and non-ionized electrolyte, has been put forward.[1] In the case of some electrolytes the values of B indicate that the dissolved electrolyte has the same volume as the solid salt, whilst salts forming hydrates in the solid state are hydrated in solution. Some electrolytes do not comply with the equation; the anomalies are traced to complex ions or the affinity of the salts for water. The density increase is greater the greater the sum of the mobilities of the constituent ions.

Von Hevesy[2] assumes that ions, or dispersed charged particles, tend to exhibit a constant potential difference between themselves and the solvent, amounting to about 70 millivolts. Ions with smaller radii will attach water molecules till this gives a radius of 2.8×10^{-8} cm. The solvent is contracted. If the size of the ion is increased beyond this by hydration, the mobility is reduced, since the P.D. is also reduced. Lorenz[3] has criticized the theory; it holds only for organic ions with 27 atoms. Those with fewer atoms have a smaller, those with more a larger, radius than 2.8×10^{-8} cm and there is no discontinuity in passing through this point.

Influence of Temperature on Conductivity: The specific conductance κ increases, usually, about 2 per cent per degree rise in temperature in aqueous solutions. Kohlrausch[4] represents the effect by the formula.

$$\kappa_t = \kappa_{18}[1 + \alpha(t - 18) + 0.0177(\alpha - 0.0177)(t - 18)^2],$$

where κ_t and κ_{18} are the conductivities at $t°$ C. and 18° C., and α is a specific constant which, in very dilute solutions, varies from 0.163 for HNO_3 to 0.0262 for Na_2CO_3.[5]

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[1] Magie, *Phys. Rev.*, **25**, 171 (1909), Heydweiller, *Ann. Physik*, **30**, 873 (1909), *Z. anorg. Chem.*, **116**, 42 (1921) (tables of A and B), Clausen, *Ann. Physik*, **44**, 1067 (1914), **37**, 51 (1912), finds that with rise of temperature, A/B tends to the same value for all electrolytes.

[2] *Jahrb. Radioakt. Elektronik*, **2**, 419 (1911), **13**, 273 (1916).

[3] *Z. anorg. Chem.*, **105**, 175 (1919), cf. von Hevesy, *Kolloid Z.*, **21**, 129 (1917).

[4] *Sitz. ber. Preuss. Akad.*, 1026 (1901), 572 (1902).

[5] Temperature coefficients, see Kolrausch and Holborn, Leitvermögen, p. 146 ff.; Kohlrausch and Grotrian, *Ann. Physik*, **154**, 1, 215 (1875), Grotrian, **151**, 378 (1874), on fluidity, *ibid.*, **157**, 130 (1876), **160**, 238 (1877), **8**, 529 (1879), Kohlrausch, *ibid.*, **159**, 233 (1876); Otten, *Diss.*, *Munich* (1887), Sack, *Ann. Physik*, **43**, 212 (1891), Holland, *ibid.*, **50**, 349 (1893), Beetz, *ibid.*, **117**, 1 (1862); Vincentini, *Atti Torino*, **20**, 869 (1885); Krannhals, *Z. physik. Chem.*, **5**, 250 (1890); Arrhenius, *ibid.*, **1**, 631 (1887), **4**, 96 (1889); **8**, 419 (1891); **9**, 339 (1892); Schaller, *ibid.*, **25**, 497 (1898), H. Jahn, *ibid.*, **16**, 72 (1895); Rudolphi, *ibid.*, **17**, 277 (1895); Dorn and Vollmer, *Ann. Physik*, **60**, 468 (1897), W. Foster, *Phys. Rev.*, **8**, 257 (1899), Kahlenberg, *J. Phys. Chem.*, **5**, 339 (1901); H. C. Jones and Douglas, *Am. Chem. J.*, **26**, 428 (1900); Lyle and Hosking, *Phil. Mag.*, **3**, 487 (1902), Hulett and Allen, *J. Am. Chem. Soc.*, **24**, 667 (1902); Hantzsch and Davidson, *Ber.*, **31**, 1612 (1898); Dennhardt, *Ann. Physik*, **67**, 325 (1899), A. A. Noyes, *Pub.* **63**, *Carnegie Inst. Washington*, 1907; Noyes

A more accurate form of Kohlrausch's equation is:

$$\kappa_t = \kappa_{18}[1 + \alpha(t - 18) + 0.0163(\alpha - 0.0174)(t - 18)^2].^1$$

The equations may be applied to incompletely ionized electrolytes with close approximation.[2] Arrhenius pointed out that in such cases the heat of ionization is involved, and in some instances the decrease of ionization with rise of temperature may outweigh the increase of mobility, when a negative temperature coefficient results (e.g., phosphoric and phosphorous acids), and a maximum conductivity is reached at a particular temperature.[3] This is generally found also at high temperatures.[4] The temperature of the maximum is lower the more concentrated the solution. The work of Noyes and his collaborators showed that the higher the conductance of the solution the lower the temperature of the maximum and the lower the concentration at which the maximum appears at a given temperature. The more complex the salt the lower the temperature and the lower the concentration at which the maximum appears. For strong acids the maxima lie at temperatures considerably below those of binary salts. The ionization of strong electrolytes, apparently without exception, decreases with rise of temperature, but at lower temperatures the rate of decrease is relatively small. In the case of weak acids and bases the ionization increases between 0° and 40° and then decreases rapidly at higher temperatures. Sulphuric acid, which ionizes in stages, exhibits peculiarities at different concentrations. The ionization constant of

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and Coolidge, *Z. physik. Chem.*, **46**, 323 (1903) (NaCl and KCl to 306°); Kato, *Mem. Coll. Sci. Eng. Kyoto*, i, 332 (1908) (H_2SO_4 to 218°); Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 454 (1912) (0° and 18°); Noyes and Johnston, *ibid.*, **31**, 987 (1909); Johnston, *ibid.*, **31**, 1010 (1909) (to 156°); Noyes, Kato and Sosman, *Z. Physik Chem.*, **73**, 1 (1910) (to 306°); Noyes, Melcher, Cooper and Eastman, *ibid.*, **70**, 335 (1909) (to 306°); Clausen, *Ann. Physik*, **37**, 51 (1911); H. C. Jones, *Pub.* **170**, *Carnegie Inst. Washington*, 1912 (0° to 65°); Jones and Getman, *Z. physik. Chem.*, **49**, 385 (1904); Jones and Jacobson, *ibid.*, **40**, 355 (1908), Jones and West, *Am. Chem. J.*, **34**, 357 (1905); **44**, 481 (1911); Jones and White, *ibid.*, **42**, 520 (1909); Jones and Howard, *ibid.*, **48**, 500 (1913); Jones and Winston, *ibid.*, **46**, 368 (1912); Bartoli, *Rend. Inst. Lombard.*, **28**, 246 (1895); Baur, *Z. physik. Chem.*, **23**, 409 (1897); Bousfield and Lowry, *Proc. Roy. Soc.*, **71**, 42 (1903); Déguisne, *Diss., Strasburg*, 1895; Euler, *Z. physik. Chem.*, **21**, 257 (1896); Felipe, *Physik. Z.*, **6**, 422 (1905); Gnesotto, *Atti Inst. Veneto*, **59**, ii, 987 (1900); Hechler, *Ann. Physik*, **15**, 157 (1904); Hunt, *J. Am. Chem. Soc.*, **33**, 795 (1911); Kunz, *Z. physik. Chem.*, **42**, 591 (1903); Lussana, *Atti Inst. Veneto*, **4**, 1466 (1893); Müller, *Bull. Soc. Chim. France*, **11**, 1001 (1912); Rasch and Hinrichson, *Z. Elektrochem.*, **14**, 46 (1908); Whetham, *Phil. Trans.*, **194**, 321 (1900); *Proc. Roy. Soc.*, **71**, 332 (1903); Wörmann, *Ann. Physik*, **29**, 194, 623 (1909); Wood, *Z. physik. Chem.*, **18**, 521 (1895); Normand, *J. Chem. Soc.*, **107**, 285 (1915).

[1] Luther, in Winkelmann's Physik, IV, i, 425.

[2] Arrhenius, *Z. physik. Chem.*, **4**, 96 (1889); **9**, 339 (1892); Euler, *ibid.*, **21**, 257 (1896); Rivals, *Compt. rend.*, **125**, 574 (1897); Steinwehr, *Z. physik. Chem.*, **38**, 185 (1901); Kortright, *Am. Chem. J.*, **18**, 365 (1896); Hantzsch, *Ber.*, **32**, 3066 (1899); Guichard, *ibid.*, **32**, 1723 (1899); Abegg, *ibid.*, **33**, 393 (1900); Jaeger and Kapma, *Z. physik. Chem.*, **113**, 27 (1920) (accurate measurements to 1600° with fused salts).

[3] Cf. Sack, *Ann. Physik*, **43**, 212 (1891); Jones and MacKay, *Am. Chem. J.*, **19**, 83 (1897).

[4] Maltby, *Z. physik. Chem.*, **18**, 133 (1895); Hagenbach, *Ann. Physik*, **5**, 276 (1901); Kramers, *Arch. Néerl.*, **1**, 455 (1898); especially the work of Noyes and collaborators in preceding references.

water, $K_w = [H^{\cdot}][OH']$, increases very rapidly at lower temperatures, passing through a maximum about 218°, and then decreases:

	0°	18°	25°	100°	156°	218°	306°
$K_w \times 10^{14}$	0.089	0.46	0.82	48	223	461	168

The results with salts at high temperatures may be affected by hydrolysis.

Larmor[1] suggests that the temperature expression $1 + \alpha t + \beta t^2$ may be factorized: $(1 + at)(1 + bt)$, and considers that a expresses the effect on the viscosity of the solvent, and b that on the electrolyte. Lyle and Hosking[2] showed that the equivalent conductance and fluidity of solutions of NaCl, when plotted against temperature, give similar but not identical curves, which indicate that both Λ and fluidity would vanish at − 35.5° C. Rasch and Hinrichsen[3] suggest the relation $\log \kappa = -\gamma/T + C$, where γ and C are constants.

Kohlrausch's Law: A simple relation between values of Λ_∞ for various salts in dilute solution was discovered by F. Kohlrausch[4] in 1875, and confirmed by later more accurate measurements.[5] The following table gives values of Λ_∞ for two pairs of salts with common ions:

	K	Na
Cl	130.10	108.99
NO_3	126.50	105.33

The values ($KCl - KNO_3$) and ($NaCl - NaNO_3$) are 3.60 and 3.66, respectively; those of ($KCl - NaCl$) and ($KNO_3 - NaNO_3$) are 21.11 and 21.17, respectively. The difference for two kations is independent of the anions, and *vice versâ*. The relation, which is perfectly general in very dilute solutions, shows (as Kohlrausch pointed out in 1875) that the limiting equivalent conductance of a salt is additively composed of two parts, the first depending only on the kation and the second only on the anion. This indicates that in solution the two ions move independently. Thus we can always write:

$$\Lambda_\infty = {}_\infty l_a + {}_\infty l_k$$

The terms ${}_\infty l_a$ and ${}_\infty l_k$ are called by Kohlrausch the *mobilities* of anion and kation, respectively. The equivalent conductance at infinite dilution is the sum of the mobilities of anion and kation at a given temperature.

When values of Λ_∞ are known, the value of *one* mobility will enable all the rest to be calculated. The mobility is closely related to the Hittorf migration ratio, which gives the fraction of the total current carried by the ion, as will be explained later. Since the migration ratio of KCl is practically independent of temperature and concentration, it was taken by Kohlrausch as the basis of his calculations. By a small extrapolation he found, at 18°,

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[1] *Phil. Trans.*, **204**, 296 (1904).

[2] *Phil. Mag.*, **3**, 487 (1902).

[3] *Z. Elektrochem.*, **14**, 41 (1908). temperature effect with feeble acids, see Mandala, *Gaz. chim. ital.*, **46**, 298 (1916).

[4] *Göttinger Nachr.*, p. 213 (1876).

[5] Kohlrausch, *Ann. Physik*, **50**, 385 (1893); **66**, 785 (1898); *Sitz. ber. preuss. Akad. Wiss.*, 581 (1902); Leitvermögen, 1916, p. 104.

$$_{\infty}l_k/_{\infty}l_a = 0.479/0.503.$$

Hence, $_{\infty}l_{K^{\cdot}} = 0.497 \times 130.10 = 64.6$, and $_{\infty}l_{Cl'} = 0.503 \times 130.10 = 65.5$. Thence, the values of the mobilities in the following table, referring to 18°, were calculated from the values of Λ_{∞} for the salts. The table includes also the values of Noyes and Falk[1] whenever possible. Starred values are uncertain.

TABLE III

MOBILITIES OF IONS AT 18° C.

	l	$c \times 10^4$		l	$c \times 10^4$		l	$c \times 10^4$
$Li^{\cdot}$	33.3	265	SCN'	56.7	221	$\frac{1}{2}Mg^{\cdot\cdot}$	45.9	256
$Na^{\cdot}$	43.4	244	$C_5H_9O_2'$	25.7	244	$\frac{1}{2}Zn^{\cdot\cdot}$	47.0	254
F'	46.6	238	CHO_2'	47*	—	$\frac{1}{2}Cu^{\cdot\cdot}$	45.9	—
$Ag^{\cdot}$	54.0	229	$C_2H_3O_2'$	35*	238	$\frac{1}{2}Cd^{\cdot\cdot}$	46.4	245
$K^{\cdot}$	64.6	217	$C_3H_5O_2'$	31*	—	$\frac{1}{2}Sr^{\cdot\cdot}$	51.9	247
Cl'	65.5	216	IO_3'	34.0	234	$\frac{1}{2}Ca^{\cdot\cdot}$	51.9	247
$Tl^{\cdot}$	65.9	215	ClO_3'	55.1	215	$\frac{1}{2}Ba^{\cdot\cdot}$	55.4	239
I'	66.6	213	BrO_3'	47.6	—	$\frac{1}{2}Pb^{\cdot\cdot}$	60.8	240
Br'	67.7	215	IO_4'	48	—	$\frac{1}{2}Ra^{\cdot\cdot}$	58*	239
$Rb^{\cdot}$	67.5	214	ClO_4'	64	—	$\frac{1}{2}C_2O_4''$	63.0	231
$Cs^{\cdot}$	68	212	NO_3'	61.8	205	$\frac{1}{2}SO_4''$	68.5	227
$H^{\cdot}$	313.9[2]	154	OH'	174	180	$\frac{1}{2}CrO_4''$	72*	—
$NH_4^{\cdot}$	64.7	222	$\frac{1}{2}Ni^{\cdot\cdot}$	44	—	$\frac{1}{2}CO_3''$	60*	270
$\frac{1}{2}Be^{\cdot\cdot}$	28	—	$\frac{1}{2}Fe^{\cdot\cdot}$	45	—	$\frac{1}{4}Fe(CN)_6''''$	95.0	—
$\frac{1}{2}Mn^{\cdot\cdot}$	44	—	$\frac{1}{3}Fe^{\cdot\cdot\cdot}$	61	—	$\frac{1}{3}Al^{\cdot\cdot\cdot}$	40	—
$\frac{1}{2}Co^{\cdot\cdot}$	43	—	$\frac{1}{3}Cr^{\cdot\cdot\cdot}$	45	—	$\frac{1}{3}La^{\cdot\cdot\cdot}$	61.0	—
						$\frac{1}{3}Sm^{\cdot\cdot\cdot}$	53.5	—
						$\frac{1}{4}Th^{\cdot\cdot\cdot\cdot}$	23.5	—

The values of c are temperature coefficients, i.e., $(l_{t_2} - l_{t_1})/(t_2 - t_1)l$, where $l = (l_{t_1} + l_{t_2})/2$. From these the values at other temperatures than 18° may be calculated.

The physical meaning of Kohlrausch's law is clear from the point of view of the ionic theory: the conductivity is due only to the free ions, and is additively composed of the terms due to the latter. By addition of the values for $H^{\cdot}$ and $C_2H_3O_2'$, for example, we obtain the value of Λ_{∞} for the weak acid CH_3COOH, which cannot be obtained directly. The values for the anions of weak acids and for the kations of weak bases may be found from the values of Λ_{∞} for salts, since nearly all salts, even of weak acids and bases, are highly ionized at high dilutions. Thus, Λ_{∞} for acetic acid = 313.9 + 35 = 348.9.

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[1] *J. Am. Chem. Soc.*, **34**, 454 (1912).

[2] Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

The mass law

$$(\Lambda/\Lambda_0)^2c/(1 - \Lambda/\Lambda_0) = \text{const.}$$

leads to the following equation for a weak electrolyte:

$$\Lambda_0 = \Lambda\Lambda_1(c\Lambda - c_1\Lambda_1)/(c\Lambda^2 - c\Lambda_1^2),$$

where Λ and Λ_1 are the equivalent conductances at concentrations c and c_1. Derick[1] points out that if the value so calculated for a weak acid such as acetic is in agreement with that calculated by subtracting ${}_0l_{\text{Na}^\cdot}$ from Λ_0 for the sodium salt, and adding to ${}_0l_{\text{H}^\cdot}$, the same value of Λ_0 should be found by the latter process as by the above method. This provides a check on the value of ${}_0l_{\text{H}^\cdot}$, and also serves to indicate whether a "water correction" is necessary in the case of organic acids and transition electrolytes.

The values of l for $\text{H}^\cdot$ and OH' are seen to be of great importance. They are noticeably higher than those for other ions, and their determination is difficult. Noyes and Sammet[2] give 329.8 at 18° for $\text{H}^\cdot$, and 174 for OH'. Kendall[3] gives for $\text{H}^\cdot$ the values 313.9 ± 0.4 at 18°, and 347.2 ± 0.4 at 25°. A large number of values for inorganic and organic ions are given by Bredig. These[4] require multiplication by 1.066 to reduce to ohm^{-1}. They refer to 25°.

When the solutions are not very dilute, Kohlrausch's law no longer holds. The deviations may be assumed due to incomplete ionization:[5]

$$\Lambda = \alpha({}_\infty l_a + {}_\infty l_k).$$

Hence,

$$\alpha = \Lambda/\Lambda_\infty.$$

The mobilities are here assumed constant, and since the conductance is proportional to the number of ions, the rate at which they move, and their charges, the changes of conductance are referred solely to changes in the number of ions. Another way is to assume the conductance always the sum of the mobilities, the latter varying with dilution.

$$\Lambda = l_a + l_k.$$

This probably holds good at all concentrations, and gives the surest[6] form of Kohlrausch's theory. It will be noticed that α cannot be found unless the mobilities are assumed constant, or the changes with dilution are known.

The calculation of α from conductivities when ionization occurs in stages, e.g., $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^\cdot + \text{HSO}_4' \rightleftharpoons 2\text{H}^\cdot + \text{SO}_4''$, requires special consideration, and will be taken up later.[7]

[1] *J. Am. Chem. Soc.*, **36**, 2268 (1914).

[2] *Z. physik. Chem.*, **43**, 49 (1903).

[3] *J. Chem. Soc.*, **101**, 1275 (1912), with discussion of previous values.

[4] *Z. physik. Chem.*, **13**, 191 (1894).

[5] Ostwald, *Z. physik. Chem.*, **2**, 840 (1888).

[6] Whetham, Theory of Solution, 1902, p. 226.

[7] See p. 549; Harkins, *J. Am. Chem. Soc.*, **33**, 1836 (1911).

Absolute Mobilities: From the values of l_a and l_k expressed in ohm^{-1} it is possible to calculate the absolute velocities in cm. per sec. under a potential gradient of 1 volt per cm., represented by v and u, or under a force of 1 dyne, represented by V, U.[1] Consider the solution in a centimeter cube with electrodes at opposite faces, and let there be a P.D. of 1 volt between the electrodes (Fig. 12). The current through the cell will be the specific conductance, κ ampère. Let the concentration η be so small that the solute is completely ionized, then the number of coulombs transported per second is·

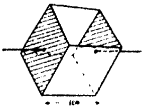

FIG. 12

$$\kappa = \eta\Lambda_\infty = \eta({}_\infty l_a + {}_\infty l_k).$$

Let u and v be the velocities in cm. per sec. per volt per cm., for kation and anion, respectively. All kations in a length u of the cube will have moved through a given section in 1 second, and similarly all the anions in a length v. These are $u\eta$ gm. equiv. and $v\eta$ gm. equiv., respectively. Each equivalent transports 96,500 coulombs, hence the transport in both directions per second will be $96{,}500(u + v)\eta$. This is the total current, hence:

$$\eta({}_\infty l_k + {}_\infty l_a) = 96{,}500\eta(u + v);$$

$\therefore u = 0.0_41036\ {}_\infty l_k$ and $v = 0.0_41036\ {}_\infty l_a$ in cm./sec. per volt/cm.

To find U and V we remember that 1 electromagnetic unit of quantity is 10 coulombs, and that 1 volt is 10^8 E.M.U. The work done in transporting 1 gm. equiv. 1 cm. under a P.D. of 1 volt/cm. is thus 9650×10^8 ergs, and the force acting on it is 9650×10^8 dynes. The force and velocity are proportional, on account of the viscous drag, hence the forces required to impart unit velocity to each ion are $9650 \times 10^8/u$ and $9650 \times 10^8/v$, respectively. The velocities under unit force (1 dyne) are thus:

$$U = u/9650 \times 10^8 \text{ cm./sec.,} \qquad \text{and} \qquad V = v/9650.10^8 \text{ cm./sec.}$$

Since 1 gram weight is 981 dynes, the forces in kgm. wt. to impart unit velocity are $9.8 \times 10^5/u$ and $9.8 \times 10^5/v$. If M is the equivalent weight, the forces per gram of ion are $9.8 \times 10^5/M_1u$ and $9.8 \times 10^5/M_2v$. To impart unit velocity to 1 gram of potassium ions requires a force of 38,000,000 kgm. wt. This explains the extreme slowness of motion of ions in solution. From the values of l_k and l_a the velocities of $K^\cdot$ and Cl' ions under a potential gradient of 1 volt/cm. are calculated from the above equations as 0.00066 cm./sec., and 0.00067 cm./sec., respectively.

The force required to impart unit velocity to a single ion is $9.8.10^5/N_0u$ kgm. wt., where N_0 = Avogadro's constant. For the $K^\cdot$ ion this is 2.5×10^{-9} milligram weight.

The Migration of Ions: Transport Number. Indications that ions move at unequal rates in electrolysis had been obtained by Gmelin,[1] and especially by Daniell and Miller,[2] but on account of the great experimental difficulties no reliable information was available until the work of Hittorf,[3] begun in 1853.

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[1] Kohlrausch, *Ann. Physik*, 6, 196 (1879); Leitvermögen, p. 105; Budde, *Ann. Physik*, 156, 618 (1875).

The principle of the method is seen from Fig. 13. The trough *AB* is divided by partitions *C* and *D*, either real (apparatus with diaphragms) or imaginary (apparatus without diaphragms), into three parts. These diaphragms are perfectly permeable and their object is to prevent mixing of the liquids by diffusion. Let the trough be filled with an electrolyte, say HCl, the ions of which move with speeds in the ratio $H^{\cdot}/Cl' = 5/1$. Let 1 *F* be passed through from electrodes *A* and *B*. The following changes occur:

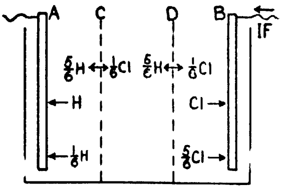
A
C
D
B
IF
$\frac{5}{6}H \leftrightarrow \frac{1}{6}Cl$
$\frac{5}{6}H \leftrightarrow \frac{1}{6}Cl$
←H
Cl→
←$\frac{1}{6}$H
$\frac{5}{6}$Cl→

FIG. 13

(i) *In AC.* Total loss of $H^{\cdot}$ = 1 equivalent, of which 5/6 migrated in from *CD* and hence 1/6 was taken from *AC*. Also 1/6 Cl' has migrated from *AC* to *CD*. Thus 1/6 mol. HCl is lost from *AC*.

(ii) *In CD.* There is a migration of 5/6 $H^{\cdot}$ from *BD* and 5/6 $H^{\cdot}$ to *AC*. Also 1/6 Cl' migrates in from *AC* and 1/6 Cl' out to *BD*. Total loss nil.

(iii) *In BD.* Total loss of Cl' is 1 equivalent, of which 1/6 migrates in from *CD* and 5/6 therefore come from *BD*. Also 5/6 $H^{\cdot}$ migrate out of *BD* to *CD*. The total loss of HCl from *BD* is 5/6 mol.

The losses in *neutral electrolyte molecules* (HCl) round the electrodes are in the ratio of the velocities of the ions moving away from the electrodes. This result is easily generalized.[4]

If in electrolysis 1 equivalent of kation is deposited, a fraction *n* is taken from the immediate vicinity of the electrode, and the fraction $(1 - n)$ migrates into the kathode space from the bulk of the solution. Thus *n* equivalents of anion must migrate out of the kathode space to make up the total charge *F* crossing any section of the electrolyte. The current is carried by anions and kations in the ratio $n : (1 - n)$. The fraction *n* was called by Hittorf the *transport number* of the anion. The transport number of the kation is $1 - n$.

If l_k, l_a are the mobilities of the two ions, then, by definition:

$$l_k/l_a = (1 - n)/n.$$

This gives the ratio of l_k/l_a when *n* is known; their sum is equal to Λ, hence l_k and l_a may be calculated separately.[5]

There is never the slightest separation of the ions in the bulk of the solution, and the result is independent of the ultimate fate of the ions which move.[1]

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[1] *Ann. Physik*, **44**, 30 (1838).

[2] *Phil. Trans.*, **134**, 1 (1844).

[3] *Ann. Physik*, **89**, 177 (1853), **98**, 1 (1856); **103**, 1 (1858), **106**, 337, 513 (1859); reprinted in Ostwald's *Klassiker*, Nos. 21 and 23, *Leipzig*, 1891, *Ann. Physik*, **4**, 374 (1878); *Z. physik. Chem.*, **39**, 613 (1901), **43**, 239 (1903), Hittorf and Salkowski, *ibid*, **28**, 546 (1899).

[4] See Larmor, Æther and Matter, Cambridge, 1900, p. 290.

[5] F. Kohlrausch, *Götting. Nachr.*, 1876, p. 213; cf. pp. 539, 540.

In the case of mixed electrolytes, Hittorf assumed that they carry the current in the ratio of their conductivities. The detailed calculation, which involves the theory of ionization, shows that the quantity of any ion passing a cross section is proportional to its concentration in the mixture and to its mobility.[2]

Determination of Transport Numbers: In the determination of transport numbers the possibility of the existence of complex ions must be kept in mind, and, if these are present, the transport of one ion only will not give correct results. In some cases the metal ion may unite with salt, or a complex anion may be formed, by which metal is carried to the anode. The presence of complex ions may be detected by transport measurements.[3]

The principal types of apparatus used are shown in Fig. 14. Type *a*, used by Hittorf, is provided with membranes; the anode, usually cadmium, is in the lower vessel, and the platinum kathode in the upper. The membranes are not without influence on the results,[4] and are not now used. Apparatus *b*, used by Hittorf, Lenz,[5] Hopfgartner,[6] Jahn[7] and Rieger,[8] is provided with a glass plug for separating the anode and kathode spaces after the experiment, and is a good type. Type *c* is a simple one used by Weiske,[9] Lussana,[10] Hellwig,

[1] Hittorf, *Ann. Physik*, **103**, 1 (1858). See also Whetham, *Phil. Trans.*, **184**, 337 (1893); *Z. physik. Chem.*, **11**, 220 (1893); Kohlrausch, *Ann. Physik*, **62**, 209 (1897); Weber, *Z. physik. Chem.*, **4**, 182 (1889); *Sitz. ber. preuss. Akad.*, p. 567 (1897); Masson, *Phil. Trans.*, **192**, 331 (1899); *Z. physik. Chem.*, **29**, 501 (1899); Steele, *ibid.*, **40**, 689 (1902); Abegg and Gauss, *ibid.*, **40**, 737 (1902); Kümmel, *Ann. Physik*, **46**, 105 (1892); Zahn, *ibid.*, **48**, 606 (1893); Lorenz and Posen, *Z. anorg. Chem.*, **95**, 340 (1916).

[2] Stackelberg, *Z. physik. Chem.*, **23**, 493 (1897); Hopfgartner, *ibid.*, **25**, 115 (1898); Hoffmeister, *ibid.*, **27**, 345 (1898); Schrader, *Z. Elektrochem.*, **3**, 498 (1897), Rieger, *ibid.*, **7**, 863 (1901); Pfanhauser, *ibid.*, **7**, 698 (1901); Hellwig, *Z. anorg. Chem.*, **25**, 157 (1901); McGregor and Archibald, *Phil. Mag.*, **45**, 151 (1898); Braley and Hall, *J. Am. Chem. Soc.*, **42**, 1770 (1920); Schneider and Braley, *ibid.*, **45**, 1121 (1923).

[3] Hittorf, *Ann. Physik*, **106**, 513 (1859); Rosenheim, *Z. anorg. Chem.*, **11**, 175 (1896); Kistiakowski, *Z. physik. Chem.*, **6**, 97 (1890); Hellwig, *Z. anorg. Chem.*, **25**, 157 (1901); Morse, *Z. physik. Chem.* **41**, 709 (1902); Kremann, *Z. anorg. Chem.*, **33**, 87 (1903); **35**, 48 (1903); Bredig, *ibid.*, **34**, 202 (1903); Coehn, *Ber.*, **35**, 2673 (1902); Whetham, *Phil. Trans.*, **184**, 358 (1893); Steele, *ibid.*, **198**, 133 (1902); Schlundt, *J. Phys. Chem.*, **6**, 159 (1902); Heym, *Ann. Physique*, **12**, 443 (1919), Falk, *J. Am. Chem. Soc.*, **32**, 1555 (1910); Braley and Hall, *ibid.*, **42**, 177 (1920); Hixon, *Medd. K. Vetensk. Nobel Inst.*, **4**, No. 12 (1922); Schneider and Braley, *J. Am. Chem. Soc.*, **45**, 1121 (1923); Bray and Mackay, *ibid.*, **32**, 914 (1910); Sandonnini, *Gazetta*, **46**, ii, 205 (1916); Lorenz and Posen, *Z. anorg. Chem.*, **95**, 340 (1916); Drucker, *Z. Elektrochem.*, **18**, 236 (1912); Costachescu and Apostoi, *Ann. Sci. Univ. Jassy*, **7**, 101 (1912); Jaques, Complex Ions, 1914, Chap. III.

[4] Bein. *Z. physik. Chem.*, **28**, 439 (1898); Hittorf, *ibid.*, **39**, 613 (1901); **43**, 239 (1903).

[5] *Ann. Physik Beibl.*, **7**, 399 (1883).

[6] *Z. physik. Chem.*. **25**, 119 (1898).

[7] *Z. physik. Chem.*, **37**, 673 (1901); **38**, 127 (1902).

[8] *Z. Elektrochem.*, **7**, 863 (1901).

[9] *Ann. Physik*, **103**, 466 (1858).

[10] *Atti. Inst. Veneto*, **3**, 1111 (1892); **4**, 1563 (1893).

Rieger, and Mather,[1] in which the spaces are separated by a wide stopcock. In type *d*, used by Wiedemann[2] and Kirmis,[3] the separation is effected by letting air into the siphon. Type *e* was used by Noyes.[4] After electrolysis the ends are closed and liquid pipetted from the upper tubulures. During electrolysis Noyes kept the liquids round the electrodes constantly neutral by adding acid or alkali. In types *f*, *g*, and *h*, used by Nernst and Loeb (type *g* modified),[5] Bein (type *h* modified),[6] Kistiakowski (type *g*),[7] Carrara (type *h*)[8] and Denison and Steele (type *f*),[9] the liquids may be run out and weighed. Type *h* is a good one. The object of the bulbs is to decrease resistance, which causes heating and convection currents.

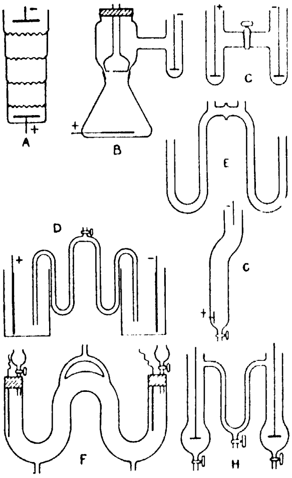

Fig. 14. Types of Transport Number Apparatus

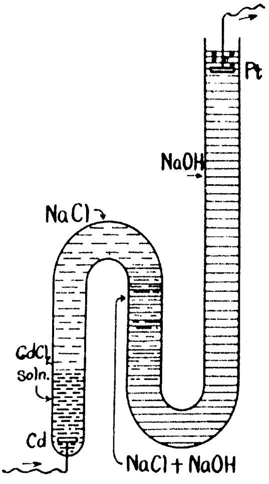

Fig. 15. Hittorf's Transport Number Apparatus

Hittorf[10] used the apparatus shown in Fig 15. Cadmium is used for the anode, platinum for the kathode. The electrolyte is NaCl. $CdCl_2$ is formed at the anode, and $Cd^{\cdot\cdot}$ ions move towards the kathode, but, being slow, never catch the $Na^{\cdot}$ ions, the two layers of liquid remaining separate as shown. At the kathode, all the Cl' ions have migrated away and are replaced by OH' ions from the water, and, as these are fast ions, there is mixing, as shown. The hydrogen rises from the kathode and does not cause mixing in the bulk of the liquid.

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[1] *Am. Chem. J.*, **26**, 473 (1901).

[2] *Ann. Physik*, **87**, 321 (1852), **99**, 177 (1856)

[3] *Ann. Physik*, **4**, 503 (1878).

[4] *Z. physik. Chem.*, **36**, 63 (1901).

[5] *Z. physik. Chem.*, **2**, 948 (1888).

[6] *Ibid.*, **27**, 23 (1898).

[7] *Ibid.*, **6**, 105 (1890).

[8] *Mem. Acad. Lincei*, **4**, 338 (1901).

[9] *J. Chem. Soc.*, **81**, 456 (1902).

[10] Cf. *Ann. Physik*, **103**, 1 (1858), also Bein, *loc. cit.*

The original NaCl solution contained 0.01784 per cent Cl and was contained in an apparatus in three parts, with taps. The weights of solution in these were: anode part, 226.99 gm.; middle part, 195.24 gm.; kathode part, 331.49 gm. The weights of Cl in these before electrolysis were therefore 0.04048 gm., 0.03482 gm., and 0.05913 gm. (Note the small quantities.) The weights found after the experiment were 0.04671 gm., 0.03483 gm., and 0.05289 gm. The middle part was unchanged, the anode gained 0.00623 gm., and the kathode lost 0.00624 gm. A voltage of 150 was applied for 108 minutes, and the weight of silver deposited in a coulometer in series was equivalent to 0.01021 gm. Cl. (Note the small weights involved.) The migration ratio of Cl in NaCl is thus $0.00624/0.01021 = 0.611$. This example has been given to show the weak currents, long times, and small transports which must be used in such experiments. In Noyes' experiments, on the other hand, a current of 0.02 to 0.18 amp. was used for 7 hours, a much greater transport was obtained, and the results were correspondingly more accurate.

The following table gives some directly measured transport numbers of the anions of salts. Values marked * are less accurate. The temperature is 18° and aqueous solutions were used. The concentrations are in gm. equivalents per *liter*.[1]

TABLE IV

TRANSPORT NUMBERS OF ANIONS OF SALTS AT 18° C.

m =	0.01	0.02	0.05	0.1	0.2	0.5	1	2	5
KCl KBr NH_4Cl KI	.506	.507	.507	.508	.509	.513	.514	.515	.516*
NaCl.......	—	—	.614	.617	.620	.626	.637	.642*	.650*
LiCl.........	.63	.65	.67	.69	.71	.73	.739	.745	.774
KNO_3......	—	—	—	.497	.496	.492	.487	.479	—
$AgNO_3$....	.528	.528	.528	.528	.527	.519	.501	.476	—
KOH......	—	—	—	.735	.736	.738*	.740*	—	—
HCl	—	—	.172	.172	.172	.173	.176	.18*	.238*
$\frac{1}{2}BaCl_2$.....	.56*	.565*	.575*	.585*	.595*	.615*	.640*	.657	—
$\frac{1}{2}CdI_2$	.56	.59	.64	.71*	.83*	1.00*	1.12	1.22–2.5	—
$\frac{1}{2}CuSO_4$	—	.62	.626	.632	.643	.668	.696	.720	—

In the case of uni-univalent salts the ratio is not very dependent on concentration to about 0.2 *n.*, indicating a practically constant ratio of l_a and l_k.

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[1] Kohlrausch and Holborn, Leitvermögen, pp. 213 ff.; Luther, Winkelmann's Physik, IV, i, 889 ff.

Sodium salts are less constant than potassium salts. Silver nitrate, which has been very carefully investigated, also shows constant results. Acids and bases with univalent ions give constant ratios up to about 0.2 *n*.[1] Other salts show deviations even at 0.01 *n*. Cadmium iodide exhibits a strong tendency to complex ion formation, giving a value of *n* ultimately greater than unity. Sulphates give less constant values than halogen salts, indicating greater tendency to complex formation.[2]

The Moving Boundary Method: Lodge[3] filled a tube with saline jelly, to which phenolphthalein was added, colored red by a trace of alkali. One end was in contact with dilute acid, and on passing a current the color was progressively bleached, and from the rate of motion of the boundary the velocity of $H^{\cdot}$ was found to be 0.0025 cm. sec. per volt/cm., as compared with 0.0032 from Kohlrausch's method and the transport number. Another method in which copper ions were driven through a solution just so fast that they were able to carry the current without deposition of hydrogen was used by C. L. Weber.[4]

Lodge's method was improved by Whetham,[5] who used two solutions with a common ion, with the same concentrations and nearly the same specific conductances, but different in color and density, stratified in a vertical tube (Fig. 16). In one case 0.1 *n*. $K_2Cr_2O_7$ and K_2CO_3 were used. The colored ion moved and the rate of motion of the boundary could be followed. Addition of agar did not affect the results, and the Lodge method could be used. The gradient of potential was constant through the tube, and from the measured current and the motion of the boundary the mobilities could be calculated They agreed with Kohlrausch's values.

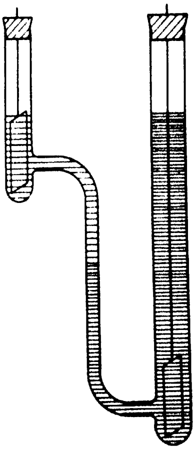

FIG. 16. Whetham's Apparatus for Moving Boundary Measurements.

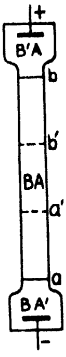

FIG. 17

The general theory of the method is as follows.[6] A solution of the salt *AB* investigated is stratified between solutions of salts *B'A* and *BA'*, having the same anion and kation, respectively, and lighter and denser than *AB*, giving the boundaries a and b, which may be seen owing to the different refractive indices of the solutions, even when these are colorless.[1] After passage of the current the boundaries move to a', b'. The ratio of the distances: $aa'/(aa' + bb')$ then gives the transport number of one ion. The ions B' and A' must have smaller mobilities than B and A, respectively, in order that the boundaries may remain sharp.[2] If only one boundary is measured, the current must also be measured.

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[1] Kraus, Electrically Conducting Systems, p. 26, thinks variations at higher concentrations are connected with changes of viscosity.

[2] Kümmel, *Ann. Physik*, 64 655 (1898).

[3] *Brit. Ass. Rep.*, 1886, p. 389.

[4] *Z. physik. Chem.*, 4, 182 (1889); Sheldon and Downing, *Phys. Rev.*, 1, 51 (1893).

[5] *Phil. Trans.*, 184, 337 (1893); 186, 507 (1895); *Phil. Mag.*, 38, 398 (1894).

[6] Cf. McInnes and Smith, *J. Am. Chem. Soc.*, 45, 2246 (1923).

An error in this method was pointed out by G. N. Lewis,[3] viz., the shrinkage of a vertical column of liquid when concentration changes occur at the electrodes, causing a shift in the position of the boundary. These may be allowed for in the calculation, but the method as a whole does not seem at present to give satisfactory results.

The three methods used for the determination of transport numbers[4] are (i) the gravimetric method of Hittorf; (ii) the moving boundary method, (iii) from conductivity, making use of Kohlrausch's law. These have been fully discussed by Noyes and Falk.[5] The values from (i) and (ii) agree at 18° within 1 per cent for HCl, HNO_3, H_2SO_4, KCl, K_2SO_4 and NH_4Cl, but for other substances (i) gives results 2.5 to 3 per cent higher than (ii). Method (iii) gives results 1 to 3 per cent higher than (ii) for uni-univalent salts, and the second method is therefore suspected. In the case of almost all uni-univalent substances the values from (iii) at infinite dilution agree to about 1 per cent with those from (i) at 0.005 to 0.02 n. The difference falls outside the limits of error with other salts.

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[1] Steele, *Phil. Trans.*, **198**, 105 (1902); *Z. physik. Chem.*, **40**, 689 (1902); Steele's work was adversely criticized by Abegg and Gaus, *Z. physik. Chem.*, **40**, 737 (1902), and by Denison, *ibid.*, **44**, 575 (1903). Denison was able to improve the method to some extent, Denison and Steele, *Phil. Trans.*, **205**, 449 (1906); *Trans. Farad. Soc.*, **5**, 165 (1909); cf. Luther in Winkelmann's Physik, IV, i, 889, Nernst, *Z. Elektrochem.*, **3**, 308 (1897). The moving boundary method was also used by Masson, *Phil. Trans.*, **192**, 331 (1899); *Z. physik. Chem.*, **29**, 501 (1899).

[2] Kohlrausch, *Ann. Physik*, **62**, 209 (1897); Weber, *Sitz. Ber. Preuss. Akad.*, p. 567 (1897), *Z. physik. Chem.*, **4**, 182 (1889); Laue, *Z. anorg. Chem.*, **93**, 329 (1915); Lorenz and Neu, *ibid.*, **116**, 45 (1921); McInnes and Smith, *J. Am. Chem. Soc.*, **45**, 2246 (1923).

[3] *J. Am. Chem. Soc.*, **32**, 862 (1910), Noyes and Falk, *ibid.*, **33**, 1436 (1911), regard the method as unsatisfactory.

[4] Additional papers on apparatus and calculation of transport numbers: Findlay, *Chem. News*, **100**, 185 (1909); Chittock, *Proc. Cambridge Phil. Soc.*, **15**, 55 (1909) (very low concs.); Riesenfeld and Reinhold, *Z. physik. Chem.*, **68**, 440 (1909), Noyes and Stewart, *J. Am. Chem. Soc.*, **32**, 1133 (1910), Falk, *ibid.*, **32**, 1555 (1910); Drucker, *Z. Elektrochem.*, **17**, 398 (1911); **19**, 8 (1913); Dhar and Bhattacharyya, *Z. anorg. Chem.*, **82**, 141 (1913); *Proc. K. Akad. Wetens. Amsterdam*, **18**, 375 (1915) (at 0°); Strachan and Chu, *J. Am. Chem. Soc.*, **36**, 810 (1914); Kraus, *ibid.*, **36**, 35 (1914); Quagliariello and d'Agostino, *Atti R. Accad. Lincei*, **24**, i, 638, 772 (1915); Heydweiller, *Z. physik. Chem.*, **89**, 281 (1915); Drucker and Kršnjavi, *ibid.*, **62**, 731 (1908); Doumer, *Compt. rend.*, **146**, 329, 687, 894 (1908); Doumer and Guillos, *ibid.*, **146**, 580 (1908); C. H. Griffiths, *Proc. Phys. Soc. London*, **28**, 132 (1916); Stepnieska-Marinkovic, *Monatsh.*, **36**, 831 (1915); Hopfgartner, *ibid.*, 751 ($Fe^{\cdot\cdot\cdot}$ slightly less mobile than $Fe^{\cdot\cdot}$); Krumreich, *Z. Elektrochem.*, **22**, 446 (1916), Hevesy, *ibid.*, **27**, 21 (1921) ($H^{\cdot}$ and OH'); Baborovský, *Rec. trav. Chim.*, **42**, 229 (1923); Lorenz and Posen, *Z. anorg. Chem.*, **96**, 81 (1916); Scarpa, *Nuovo Cim.*, **3**, 308 (1912); Chandler, *J. Am. Chem. Soc.*, **34**, 662 (1912).

[5] *J. Am. Chem. Soc.*, **33**, 1436 (1911). Cf. Millar, *Z. physik. Chem.*, **69**, 436 (1909).

The migration ratios in fused salts have been investigated (see "Fused Salts"). * In fused silver iodide the current is wholly carried by the $Ag^{\cdot}$ ion;[1] in glass the kations only carry the current.[2]

Dissociation of Ternary Electrolytes: Kohlrausch[3] found that the limiting conductivity was reached at much higher dilutions in the case of salts such as $BaCl_2$ than in the case of KCl, and even higher dilutions in the case of salts like $MgSO_4$. The calculation of the ionization is complicated when it occurs in stages:

$$AB_2 \rightleftharpoons AB^{\cdot} + B'; \qquad AB^{\cdot} \rightleftharpoons A^{\cdot\cdot} + B'$$

and it may be still further complicated by the presence of complex ions. Unless the extent to which each stage proceeds is known, the conductivity gives no indication of the state of ionization, owing to the different mobilities of the various ions. The matter has been considered by several investigators.[4] Jellinek (*loc. cit.*) points out that three different mobilities are in use; these are our l, u and U. The value of u depends on the valence (charge) of the ion, that of U is independent of valence Lorenz (*loc. cit.*) shows that when an electrolyte dissociates without intermediate stages, the value of $\alpha = \mu/\mu_{\infty}$, μ being the *molar* conductance, gives correct results, whilst the ratio Λ/Λ_{∞}, Λ being the *equivalent* conductance, is equal to α only in the case of uni-univalent electrolytes.[5]

When intermediate ions are formed, however, μ/μ_{∞} no longer gives the correct value of α. In such cases the ionization constants for the separate stages must be known.[6] Consider the case of a dibasic acid:

$$H_2A \rightleftharpoons H^{\cdot} + HA' \quad \therefore \quad k_1[H_2A] = [HA'][H^{\cdot}].$$

$$HA' \rightleftharpoons H^{\cdot} + A'' \quad \therefore \quad k_2[HA'] = [H^{\cdot}][A''].$$

$\therefore k_1k_2 = [H^{\cdot}]^2[A'']/[H_2A] = k_3$, the ionization constant for H_2A:

$$H_2A \rightleftharpoons 2H^{\cdot} + A''.$$

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[1] O. Lehmann, *Ann. Physik*, **24**, 1 (1885), **38**, 396 (1889).

[2] Warburg, *Ann. Physik*, **21**, 622 (1881), Warburg and Tegetmeier, *ibid.*, **35**, 155 (1888), Tegetmeier, *ibid.*, **41**, 18 (1890). Lorenz and Fausti, *Z. Elektrochem.*, **10**, 630 (1904), Lorenz, Elektrolyse geschmolzener Salze, ii, 159 ff., found $n = 0.36$ for K in fused $PbCl_2 + KCl$, but the method is inexact. Possibly complex ions are present

[3] *Ann. Physik*, **26**, 161 (1885).

[4] Steele, *Z. physik. Chem.*, **40**, 722 (1902), Kummell, *Z. Elektrochem.*, **9**, 975 (1903), **11**, 94, 341 (1905); Noyes and Stewart, *J. Am. Chem. Soc.*, **32**, 1133 (1910), Gobel, *Z. physik. Chem.*, **71**, 652 (1910); Deakin and Rivett, *J. Chem. Soc.*, **101**, 127 (1912), Wegscheider, *Sitz. Ber. Preuss. Akad. Wien*, ii, 141 (1902), Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 485 (1912); McBain, *ibid.*, 1134, Drucker, etc., *Z. Elektrochem.*, **19**, 797 (1913); Wegscheider, *ibid.*, **20**, 18 (1914); Drucker, *ibid.*, **20**, 83 (1914). Wegscheider, *Monatsh.*, **37**, 251 (1916); Lorenz, *Z. anorg. Chem.*, **95**, 340 (1916), **106**, 49, 63 (1919), Drucker, *Z. physik. Chem.*, **96**, 381 (1920), **38**, 602 (1901), Larsson, *Z. anorg. Chem.*, **125**, 281 (1922), McBain, *Z. Elektrochem.*, **11**, 215 (1905), Jellinek, *Z. physik. Chem.*, **76**, 257 (1911).

[5] Cf. Bousfield, *Trans. Farad. Soc.*, **15**, 71 (1919).

[6] Cf. Jellinek, *loc. cit.*, Harkins, *J. Am. Chem. Soc.*, **33**, 1838 (1911).

The value of k_1 may be found from measurements of the partition coefficient between solvents, when the concentration is such that the second stage of the ionization is inappreciable,[1] or from measurements of freezing-point, and thence

$$k_1 = \alpha^2/(1 - \alpha)V,$$

assuming the mass law, or from the conductivity $\alpha = \mu/\mu_\infty$, the value of μ_∞ being extrapolated by the Ostwald-Bredig rule. The mobility of HA' may also be found from conductivity measurements with the salt MHA, and by addition of $l_{H^{\cdot}}$ the value of μ_∞ for the acid HA' may be found.[2]

The value of k_2 may be found by measurement of $H^{\cdot}$ concentration in a solution of $MHA \rightleftharpoons M^{\cdot} + HA' \rightleftharpoons M^{\cdot} + H^{\cdot} + A''$ by an electrode, or by the conductivity of MHA at very high dilutions: $MHA \rightleftharpoons M^{\cdot} + HA' \rightleftharpoons M^{\cdot} + H^{\cdot} + A''$. If

$$[A'']/[HA'] + [A''] = K,$$

then

$$\mu = l_{M^{\cdot}} + (1 - K)l_{HA'} + 2Kl_{A''} + Kl_{H^{\cdot}},$$
$$K = [\mu - (l_{M^{\cdot}} + l_{HA'})]/(l_{H^{\cdot}} + 2l_{A''} - l_{HA'}),$$

and from K we can find k_2 by Ostwald's dilution law.[3] The conductance of the acid at very high dilutions may also be determined. Then, if V is the volume containing 1 mol., then

$$k_2 = [H^{\cdot}][A'']/[HA'] = \alpha(1 + \alpha)/V(1 - \alpha),$$
$$\mu = (1 + \alpha)l_{H^{\cdot}} + (1 - \alpha)l_{HA'} + 2\alpha l_{A''},$$
$$\alpha = [\mu - (l_{H^{\cdot}} + l_{HA'})]/(l_{H^{\cdot}} - l_{HA'} + 2l_{A''}),$$

again giving k_2. Wegscheider[4] finds

$$k_2 = \alpha[\alpha^2 - k_1V(1 - \alpha)]/k_1V^2(2 - \alpha),$$

where $\alpha = \mu/\mu_\infty$. The value of k_2 may also be found from freezing point measurements.[5]

At very high dilutions we should expect such ionizations as:

$$MX_2 \rightleftharpoons MX^{\cdot} + X' \rightleftharpoons M^{\cdot\cdot} + 2X'$$

and

$$MX_3 \rightleftharpoons MX_2^{\cdot} + X' \rightleftharpoons MX^{\cdot\cdot} + 2X' \rightleftharpoons M^{\cdot\cdot\cdot} + 3X'$$

to proceed practically to completion, and since the ions $M^{\cdot\cdot}$ and $M^{\cdot\cdot\cdot}$ carry twice and three times the charge on an ion $M^{\cdot}$, we should expect the molar conductances to reach limiting values about 2 and 3 times that of the electrolyte MX, respectively. This is found. Again, since the molar conductances of salts such as $CuSO_4$ approach a value almost double that for MX, the ionization probably proceeds in one stage: $CuSO_4 \rightleftharpoons Cu^{\cdot\cdot} + SO_4''$. These results hold also in non-aqueous solvents.[1]

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[1] Rothmund and Drucker, *Z. physik. Chem.*, **46**, 827 (1903); Drucker, *ibid.*, **49**, 563 (1904).

[2] Cf. Braun, *Z. Elektrochem.*, **14**, 729 (1908).

[3] Luther, *Z. Elektrochem.*, **13**, 296 (1907).

[4] *Monatsh.*, **23**, 599 (1902).

[5] Luther, *Z. Elektrochem.*, **13**, 294 (1907); Göbel, *Z. physik. Chem.*, **71**, 657 (1910); Jellinek, *ibid.*, **76**, 257 (1911).

Hydration from Transport Experiments: If an indifferent substance is added to a solution of an electrolyte, the changes of concentration of indifferent substance around the electrodes will depend only on the transport numbers and the hydrations of anion and kation.[2] If A and K are the numbers of molecules of water bound to anion and kation, then:

$$nA - (1 - n)K = x,$$

where n is the transport number of the anion and x the number of mols. of water transported to the anode or kathode per F. If u, v are the mobilities of the kation and anion:

$$A - (u/v)K = x/n.$$

Values of x/n have been found by Buchböck,[3] Washburn,[4] and others:

	HCl	KCl	NaCl	LiCl
x/n	1.42 to 1.52	− 1.27	− 1.24	− 2.05

Remy[5] found practically the same values when the intermediate liquid was gelatinized and the changes of volume at the electrodes read off on capillary tubes. The results were corrected for electro-endosmosis, and the mobilities in the jelly were found practically the same as in solutions. On the assumption that the number of molecules of water attached to the $H^{\cdot}$ ion is 1, the relative hydrations of other ions were found to be:[6] $K^{\cdot}$, 5; $Na^{\cdot}$, 8; $Li^{\cdot}$, 14; Cl', 4.

Riesenfeld and Reinhold[7] assume that the values found in very dilute solutions are the "true" transport numbers, whilst those found in more concentrated solutions require correction for the transport of water by the ions.[8] Consider a solution of 1 equiv. of electrolyte in a mol. of water and let 1 F pass. At the anode, a mols. H_2O will now contain $1 + n$ equiv. electrolyte, where n is the "observed" transport number. In $a + x$ mols. of H_2O there will be $1 + n + (x/a)$ equiv. of electrolyte. If n_0 is the true transport number and A and K the numbers of mols. H_2O attached to anion and kation, respectively, then, as before:

$$n_0A - (1 - n_0)K = x.$$

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[1] Kraus, Electrically Conducting Systems, p. 105

[2] Nernst, *Götting. Nachr.*, 1 (1900).

[3] *Z. physik. Chem.*, **55**, 563 (1906).

[4] *Z. physik. Chem.*, **66**, 513 (1909); Washburn and Millard, *J. Am. Chem. Soc.*, **37**, 694 (1915). Baborovsky, *Rec. trav. Chim.*, **42**, 229 (1923). Riesenfeld, below.

[5] *Z. physik. Chem.*, **89**, 467, 529 (1915).

[6] Nernst, Lehrbuch, 8–10 Aufl., p. 442

[7] *Z. physik. Chem.*, **66**, 672 (1909)

[8] G. N. Lewis, *J. Am. Chem. Soc.*, **32**, 862 (1910), shows that the results of the moving boundary method, corrected for changes of volume, give the Hittorf transport numbers, not the "true" transport numbers.

If x is positive at the anode, then in $a + x$ mols. of water after electrolysis there will be $1 + n_0$ equiv. of electrolyte. Thus:

$$1 + n_0 = 1 + n + (x/a), \qquad \text{or} \qquad n = n_0 + (x/a),$$

or, if $c = 1/a$ = concentration,

$$- dn/dc = x,$$

giving x from the curve $n = f(c)$. From these curves the following conclusions may be drawn:

(i) If the anion is more mobile than the kation at high dilutions, the latter is usually more hydrated than the former.

(ii) In such a case the transport number increases at first with increasing concentration; in the opposite case it decreases.

The degree of hydration of the ion may be calculated by combining the above equation with Stokes's law for the motion of a sphere in a viscous medium.[1] The assumption is made that the hydrated ion is surrounded by a spherical shell of water molecules, the volume of which can be calculated from Stokes's law. If the volume of the ion can be neglected in comparison with that of the water (strong hydration), the volume of the latter, and thence the hydration, can be found. If l_1, l_2 are the mobilities of two ions and r_1, r_2 their radii (including water envelopes), then Stokes's law gives:

$$l_1/l_2 = r_2/r_1.$$

But if A_1, A_2 are the numbers of molecules of water attached to the ions:

$$A_1/A_2 = r_1^3/r_2^3; \qquad \text{hence} \qquad A_1/A_2 = l_2^3/l_1^3.$$

In this way the following values are found, at infinite dilution: $H^{\cdot}$, 0; OH', 10; $K^{\cdot}$, Cl', Br', I', $\frac{1}{2}SO_4''$, 20; NO_3', 25; $Ag^{\cdot}$, ClO_3', 35; $\frac{1}{2}$Cd, $\frac{1}{2}$Cu, 55; $Na^{\cdot}$, 70; Li, 150.

With increasing concentration of electrolyte the hydration decreases. A second method,[2] depending on the use of concentration cells, has given no satisfactory results.

The abnormally high mobilities of $H^{\cdot}$ and OH' ions is perhaps due, at least in part, to their low hydration. The suggestion has been made[3] that the hydrogen ion in aqueous solutions is really the oxonium ion, $H_3O^{\cdot}$, having the same relation to oxygen as $NH_4^{\cdot}$ to ammonia. Others[4] attribute the abnormal mobilities of $H^{\cdot}$ and OH' to Grotthus conduction.

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[1] Cf. Lungo, *Nuovo Cim.*, **16**, ii, 173 (1918); Lorenz, *Z. Elektrochem.*, **26**, 424 (1920); modified Stokes's law, Born, *Z. Physik*, **1**, 221 (1920); S. W. J. Smith, *Proc. Phys. Soc. London*, **28**, 16 (1916); Bousfield, *Z. physik. Chem.*, **53**, 257 (1905); *Proc. Roy. Soc.*, **74**, 563 (1905).

[2] Reinhold, *Z. Elektrochem.*, **14**, 765 (1908); cf. Riesenfeld and Reinhold, *Z. physik. Chem.*, **68**, 459 (1910). Cf. Lenard, Weick and Mayer, *Ann. Physik*, **61**, 665 (1920).

[3] Lapworth, *J. Chem. Soc.*, **93**, 2187 (1908).

[4] Danneel, *Z. Elektrochem.*, **11**, 249 (1905); Hantzsch and Caldwell, *Z. physik. Chem.*, **58**, 575 (1907); Ghosh, *J. Chem. Soc.*, **113**, 790 (1918); criticised by Kraus, Electrically Conducting Systems, p. 209.

Solvation of Ions: The theory that ions (and unionized molecules) in solution are combined with solvent is known as the Solvate Theory: hydration is a special case of solvation. A large amount of work has been done from this point of view, but the results are not very convincing.[1]

Effect of Temperature on Ionic Mobility: Kohlrausch assumed that the formulæ giving the effect of temperature on equivalent conductance can be extended to the mobilities of the separate ions.[2] For univalent ions those with small mobilities have large temperature coefficients. According to Kohlrausch[3] the following relations between the temperature coefficient α and the mobility l hold good in aqueous solutions:

$$\begin{aligned}\alpha &= 0.0136 + 0.67/(18.5 + l) = 0.0131 + 0.640/l - 6.94/l^2\\ &= 0.0065 + 0.0683(1/l)^{0.3515}\\ &= 0.0348/(ln\, l - 0.207).\end{aligned}$$

One consequence of the small temperature coefficients of very mobile ions is that, with rise of temperature, the mobilities of all ions should tend to become equal, and the transport numbers then tend to equal 0.5. The parallellism between temperature coefficients of conductance and viscosity has been referred to previously. If we calculate from the equation:

$$\kappa_t = \kappa_{18}[1 + \alpha(t - 18) + (\alpha - 0.0177).0.0177(t - 18)^2]$$

the temperature at which $\kappa_t = 0$, we find $-39°$ C. The empirical formula for the fluidity of water as a function of temperature given by Heydweiller would give infinite viscosity at $-34°$, an interesting coincidence which suggests that the mobility is perhaps that of the hydrated ion, so that there is then friction between water and water. Noyes and Falk[4] have discussed fully the effect of temperature on transport number, and conclude that if the transport number is larger than 0.5 it invariably diminishes with rise of temperature, and if it is less than 0.5 it invariably increases. This agrees with the above result.

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[1] H. C. Jones and collaborators, beginning in 1899, summarized to 1908 by Jones, *Am. Chem. J.*, **41**, 19 (1909); Jones, Hydrates in Aqueous Solutions, *Carnegie Inst. Pub.*, No. 60 (1907); Ordeman, *ibid.*, **260**, 119 (1918); criticized by Serkoff, *J. Russ. Phys. Chem. Soc.*, **42**, 1 (1910); see also Jones, etc., *Am. Chem. J.*, **49**, 265 (1913), *J. Franklin Inst.*, **173**, 217 (1912); **176**, 479, 677 (1913), The Nature of Solution, H. C. Jones, London 1917; Baur, Von den Hydraten in wassriger Losung, Stuttgart, 1903, critical summary by Dhar, *Z. Elektrochem.*, **20**, 57 (1914); the transport method is criticized by Isgarischev and Berkmann, *Z. Elektrochem.*, **28**, 40 (1922), Aschkenasi, *ibid.*, **28**, 106 (1922); Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920); Schreiner, *ibid.*, **121**, 321 (1922). Newbery, *J. Chem. Soc.*, **111**, 470 (1917), concludes from overvoltage measurements that only $H^{\cdot}$, OH', $Fe^{\cdot\cdot\cdot}$, $Ni^{\cdot\cdot}$ and $Co^{\cdot\cdot}$ (perhaps Pt, etc.) ions are hydrated, and criticizes methods of determination of hydration. At the present time it is hardly certain that ions *are* hydrated, and the extent of hydration cannot yet be expressed numerically with any accuracy.

[2] Leitvermögen, p. 128; values see this book, p. 540.

[3] *Ann. Physik*, **50**, 385 (1893); *Sitz Ber. Preuss. Akad.*, p. 581 (1902); *Proc. Roy. Soc.*, **71**, 338 (1903); *Z. Elektrochem.*, **14**, 129 (1908); Leitvermögen, p. 128; *Sitz.-ber. preuss. Akad.*, p. 1033 (1901).

[4] *J. Am. Chem. Soc.*, **33**, 1436 (1911).

Migration Ratios from Electromotive Force Measurements: It is shown in Chapter XII *that the E.M.F. of a cell of the type:*

$$\mathrm{Ag/AgNO_3\ conc.\ }c_1\mathrm{/AgNO_3\ dil.\ }c_2\mathrm{/Ag}$$

is given by:

$$E = (2RTn/F).ln(c_1/c_2),$$

where n is the transport number of the anion. Also, the E.M.F. of a cell of the type:

$$\mathrm{Ag/AgCl/KCl\ conc.\ }c_1\mathrm{/KCl\ dil.\ }c_2\mathrm{/AgCl/Ag},$$

is given by:

$$E = [2(1 - n).RT/F].ln(c_1/c_2),$$

where $1 - n$ is the transport number of the kation.

It is evident that transport numbers may be calculated from E.M.F. measurements.[1]

Diffusion of Electrolytes: The diffusion constant D of an electrolyte is connected with the mobilities of its ions by the equation:[2]

$$D_t = 0.044856 \frac{l_k l_a}{l_k + l_a}[1 + 0.0034(t - 18)],$$

where l_k, l_a are the mobilities at $t°$,[3] and D is expressed in the usual units (cm./day).

The following table[4] shows the agreement between observed and calculated values of D at 18°.

The relation $DM^{1/2}$ = const., where M = molecular weight, has been found by Thovert.[5]

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[1] Helmholtz, *Ann. Physik*, **3**, 201 (1878); *Ges. Abhandl.*, i, 840; Moser, *Ann. Physik*, **3**, 216 (1878); Kümmel, *ibid.*, **64**, 655 (1898); McIntosh, *J. Phys. Chem.*, **2**, 273 (1898); Mugdan, *Z. Elektrochem.*, **6**, 309 (1899); Kendrick, *ibid.*, **7**, 52 (1900); Gans, *Ann. Physik*, **6**, 315 (1901); Fergusson, *J. Phys. Chem.*, **20**, 326 (1916); MacInnes and Beattie, *J. Am. Chem. Soc.*, **42**, 1117 (1920); Beattie, *ibid.*, 1128; Ferguson and France. *J. Am. Chem. Soc.*, **43**, 2150 (1921); Grube and Metzger. *Z. Elektrochem.*, **29**, 17 (1923).

[2] Nernst, *Z. physik. Chem.*, **2**, 613 (1888); **4**, 129 (1889); Lehrbuch, 8–10 Aufl., 429; Arrhenius, *ibid.*, **10**, 51 (1892); Abegg and Bose, *ibid.*, **30**, 545 (1899); Euler, *Ann. Physik*, **63**, 273 (1897); Behn, *ibid.*, **62**, 54 (1897); Planck, *ibid.*, **40**, 561 (1890); Larmor, Æther and Matter, Cambridge, p. 291 (1900); *Phil. Trans.*, **185**, 815 (1894); Donnan, *Phil. Mag.*, **45**, 529 (1898); deduction, see Whetham, Theory of Solution, 1902, chap. 13.

[3] Winkelmann, Physik, IV, p. 437.

[4] Measurements by Scheffer, *Ber.*, **15**, 788 (1882); **16**, 1903 (1883); *Z. physik. Chem.*, **2**, 390 (1885); cf. also Clack, *Phil. Mag.*, **16**, 863 (1908); Vanzetti, *Atti R. Accad. Lincei*, **18**, ii, 229 (1909); Scarpa, *Nuovo Cim.*, **20**, 212 (1910); Öholm, *Medd. K. Vetensk. Nobel Inst.*, **2**, No. 22 (1912); *ibid.*, *Finske Kemistamfundets Medd.*, **30**, 69 (1921); Griffiths, *Proc. Phys. Soc. London*, **29**, 159 (1917).

[5] *Compt. rend.*, **150**, 270 (1910); attempts to determine ionic hydration from diffusion measurements have been made by McPhail Smith, *J. Am. Chem. Soc.*, **37**, 722 (1915).

TABLE V

DIFFUSION COEFFICIENTS OF ELECTROLYTES (cm./day) AT 18° C.

	D obs.	D calc.		D obs.	D calc.
HCl	2.30	2.43	KNO_3	1.30	1.39
HNO_3	2.22	2.26	NaCl	1.11	1.18
KOH	1.85	2.07	$NaNO_3$	1.03	1.13
NaOH	1.40	1.55	H.COONa	0.95	1.02
NH_4Cl	1.33	1.44	CH_3COONa	0.78	0.88

IONIC EQUILIBRIUM IN SOLUTIONS OF ELECTROLYTES

Consider the ionization of a binary electrolyte:

$$\underset{1-\alpha}{AB} \rightleftharpoons \underset{\alpha}{A^{\cdot}} + \underset{\alpha}{B'}.$$

If the volume of solution is V, and if α is the degree of ionization, the concentrations are: $[AB] = c_0 = (1 - \alpha)/V$; $[A^{\cdot}] = [B'] = c_1 = \alpha/V$. The law of mass action then gives: c_1^2/c_0 = const. $= K$, i.e.,

$$\alpha^2/(1 - \alpha)V = K. \tag{1}$$

Since $\alpha = \Lambda/\Lambda_\infty$, we find also:

$$\Lambda^2/\Lambda_\infty(\Lambda_\infty - \Lambda)V = c\Lambda^2/\Lambda_\infty(\Lambda_\infty - \Lambda) = K.$$

This equation is known as Ostwald's Dilution Law.[1] Its deduction depends on the assumptions that the solution is dilute, and that the law of mass action can be applied to charged ions.[2]

Experimental investigation of the conductivities of dilute solutions of weak organic acids[3] and weak organic bases[4] showed that the law was very satisfactorily followed. The results for acetic acid are given in Table VI, the data being from Rivett and Sidgwick,[5] and Kendall.[6]

[1] *Z. physik. Chem.*, **2**, 36 (1888); cf W. Gibbs, Scientific Papers, vol. 1; Partington, *J. Chem. Soc.*, **97**, 1158 (1910); *Trans. Farad. Soc.*, **15**, 98 (1919); Kendall, *J. Am. Chem. Soc.*, **36**, 1076 (1914); Larmor, Æther and Matter, Cambridge, p. 286 (1900).

[2] The disturbing effects of increasing concentration and increasing ionization may act in opposite directions. Wegscheider, *Z. physik. Chem.*, **69**, 603 (1909), assumes that the law holds up to concentrations of 0.03 *n*.; Wegscheider and Lux, *Monatsh.*, **30**, 411 (1909), find agreement with salts of α-naphthalenesulphonic and *p*-toluenesulphonic acids up to 0.006 *n*. Drucker, Tarle and Gomez, *Z. Elektrochem.*, **19**, 8 (1913), find that KBr obeys Ostwald's dilution law up to 0.01 *n*. Drucker, *ibid.*, **18**, 562 (1912), finds that $N(CH_3)_4Cl$ and $N(CH_3)_4Br$ obey the law up to 0.02 *n*. Holmberg, *Svensk. Kem. Tidskr.*, p. 6 (1918), thinks NaI obeys the law up to 0.05 *n* , but he did not use conductivity methods. Washburn and MacInnes, *J. Am. Chem. Soc.*, **33**, 1686 (1911), consider that the law holds only at much higher dilutions, in the case of strong electrolytes. In the case of weak electrolytes it probably holds up to about 0.1 *n*. Cf. Jones and White, *Am. Chem. J.*, **42**, 520 (1909); Jones and Wightman, *ibid.*, **46**, 56 (1911).

[3] Ostwald, *Z. physik. Chem.*, **3**, 170, 241 (1889).

[4] Bredig, *Z. physik. Chem.*, **13**, 289 (1894); Goldschmidt and Salcher, *ibid* , **29**, 89 (1899).

[5] *J. Chem. Soc.*, **97**, 734 (1910).

[6] *J. Am. Chem. Soc.*, **36**, 1069 (1914).

TABLE VI

IONIZATION OF ACETIC ACID IN AQUEOUS SOLUTION AT 25°

V = Vol. in liters of solution containing 1 mol. CH_3CO_2H.
Λ = Equivalent conductivity, in Kohlrausch units = specific conductivity/concentration in mol. per cc.
d = Density of solution (water = 1).
η = Viscosity of solution (water = 1).
α = Ionization = Λ/Λ_∞; $\alpha' = \eta\Lambda/\Lambda_\infty\eta_\infty$.

V	Λ	α	$K \times 10^6$	d	η	α'	$K' \times 10^6$	$K'' \times 10^6$
0.334	0.6186	0.001595	7.7	1.0235	1.347	0.002149	13.9	16.5
0.672	1.123	0.002896	12.5	1.0122	1.169	0.003385	17.2	18.6
0.989	1.443	0.003636	14.0	1.0084	1.112	0.004043	17.4	18.4
1.977	2.211	0.005701	16.5	1.0043	1.056	0.006020	18.3	18.8
5.374	3.804	0.009806	18.1	1.0017	1.021	0.01001	18.8	19.0
10.753	5.361	0.01382	18.0	1.0009	1.010	0.01396	18.4	18.5
24.875	8.388	0.02163	19.2	1.0004	1.004	0.02172	19.5	19.5
63.26	13.03	0.03359	18.5	1.0002	1.002	0.03366	18.6	18.6
∞	387.9	1.00000	—	1.0000	1.000	1.00000	—	—

The value of K is calculated from equation (1) above; the value α' is corrected for viscosity: $\alpha' = \eta\Lambda/\Lambda_\infty\eta_\infty$. Kendall (*loc. cit.*) assumes that the ionization involves interaction with water molecules, and writes the mass law in the form:

$$[ion]^2/[salt][water] = K'' = K'.\,1000d_0/(1000d - m/v),$$

where d_0, d are the densities of pure water and solution, and m = molar weight of solute. The values of K (from α), K' (from α'), and K'' are given in the table, and the constancy of the latter extends even to 3 *n.* concentration. The "uncorrected" law (K) holds below 0.2 *n.* with all the accuracy found in the applications of the law of mass action to any systems, and the dilution law in the case of weak electrolytes is the form of the law of mass action which is most closely followed by experiment.[1]

In the case of strong (i.e., highly ionized, as distinct from concentrated) electrolytes, however, the law fails completely. This is seen from the results in Table VII, from the figures of Kohlrausch and Maltby.[2] The value of K, the mass action "constant," varies from 0.0154 at a dilution of 10,000 liters to 2.350 at a dilution of 1 liter, an increase of 15,000 per cent. The variation of K makes one hesitate to endorse the opinion of Nernst[3] that "the practical applications of the law of mass action are hardly disturbed by these relatively trifling deviations."

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[1] Partington, *Trans. Farad. Soc.*, **15**, 98 (1919); cf. Ebert, *Jahrb. Radioakt. Elektronik*, **18**, 134 (1921).
[2] *Wiss. Abh. phys. tech. Reichsanstalt*, **3**, 157 (1900).
[3] Lehrbuch, 8-10 Aufl., p. 581.

TABLE VII

IONIZATION OF POTASSIUM CHLORIDE AT 18° C.

V lit.	Λ	$\Lambda/\Lambda_\infty = \alpha$	$1 - \alpha$	K
∞	129.91	1.0000	0.0000	-
10,000	129.07	0.9936	0.0064	0.0154
5,000	128.77	0.9912	0.0088	0.0223
2,000	128.11	0.9862	0.0138	0.0352
1,000	127.34	0.9802	0.0198	0.0485
500	126.31	0.9723	0.0277	0.0681
200	124.41	0.9577	0.0423	0.1084
100	122.43	0.9424	0.0576	0.1542
50	119.96	0.9234	0.0766	0.2221
20	115.75	0.8910	0.1090	0.3642
10	112.03	0.8624	0.1376	0.5105
5	107.96	0.8310	0.1690	0.8154
2	102.41	0.7883	0.2167	1.434
1	98.27	0.7565	0.2435	2.350

Between weak electrolytes such as acetic acid, and strong electrolytes such as potassium chloride, there are the intermediate electrolytes, such as dichloracetic acid, the values for which are given in Table VIII. The values of K θ_1 and $K'' = \theta_2$ increase steadily with concentration. Such electrolytes are satisfactorily covered by a modification of Ostwald's formula proposed by the writer[1] and by Kendall,[2] viz.,

$$\alpha^2/(1-\alpha)(V + c\alpha) = K_2. \tag{2}$$

or, with the substitution from Ostwald's formula *in the correction term only*

$$\alpha^2 (1-\alpha)V = K + k(1-\alpha)\alpha \tag{2a}$$

which is the form used by Kendall. Szyszkowski[3] deduced an equation from which the above is derived by expanding an exponential factor. Walker[4] put forward the equation:

$$\alpha^2/(1-\alpha)V = k(1-\alpha)\alpha \tag{3}$$

which differs from the above in the omission of the Ostwald constant K.

In Table VIII are given the values:

$$\phi_1 = 100\left\{0.0185 + 0.012\left(\frac{1-\alpha}{\alpha}\right)\right\},$$

$$\phi_2 = 100\left\{0.0485 + 0.017\left(\frac{1-\alpha}{\alpha}\right)\right\}$$

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[1] *J. Am. Chem. Soc.*, **97**, 1158 (1910).

[2] *J. Am. Chem. Soc.*, **101**, 1275 (1912), *Medd. K. Vetensk. Nobel Inst.*, **2**, 38 (1913); *J. Phys. Chem.*, **19**, 193 (1915).

[3] *Medd. K. Vetensk. Nobel Inst.*, **3**, Nr. 2 (1914), *ibid.*, Nr. 41 (1913) (equation 13 in this paper).

[4] *Brit. Ass. Rep.*, p. 349 (1911)

for comparison with the values of

$$\theta_1 = 100 \frac{\alpha^2}{(1 - \alpha)V} \quad \text{and} \quad \theta_2 = 100 \frac{\alpha'^2}{(1 - \alpha')V'},$$

where α, V are the uncorrected values, and α', V' are the values corrected as explained in connection with Table VI:

$$\alpha' = \Lambda\eta/\Lambda_\infty\eta_\infty; \qquad V' = 1000V \bigg/ \left(1000d - \frac{130}{V}\right).$$

TABLE VIII

IONIZATION OF DICHLORACETIC ACID AT 25° C. (KENDALL)

V lit.	Λ	α	η	d	α'	θ_1	ϕ_1	θ_2	ϕ_2
2	114.9	0.2980	1.1318	1.0263	0.3337	6.33	7.68	8.93	8.29
4	151.7	0.3935	1.0640	1.0139	0.4186	6.38	6.70	7.40	7.25
8	190.2	0.4933	1.0287	1.0067	0.5075	6.00	6.08	6.61	6.53
16	231.6	0.6007	1.0143	1.0033	0.6093	5.65	5.64	5.97	5.96
32	273.1	0.7083	1.0071	1.0016	0.7117	5.37	5.34	5.48	5.55
64	309.7	0.8032	1.0035	1.0008	0.8058	5.11	5.14	5.24	5.26
128	338.7	0.8785	1.0018	1.0004	0.8801	4.96	5.02	5.05	5.09
256	359.2	0.9315	1.0009	1.0002	0.9324	4.95	4.94	5.03	4.99
∞	385.6	1.0000	1.0000	1.0000	1.0000	—	4.86	—	4.86

The equation of Partington may be transformed without neglect of any terms into:

$$\alpha^2/(1 - \alpha)V = K + k(\alpha/V), \tag{2b}$$

which goes over into the Ostwald form as a limiting case when $\alpha = 0$, or is very small (weak electrolyte), or k is very small. An obvious generalization of this equation is:

$$\alpha^2/(1 - \alpha)V = K + k(\alpha/V)^n \quad (n = \text{const.}), \tag{4}$$

which was proposed by McDougall[1] and by Kraus and Bray.[2] The equation:

$$(c\alpha)^2/(1 - \alpha)c = K + k(c\alpha)^n$$

has been used by Falk and Noyes[3] to represent the ionization of salts; it is identical with the above. Kraus and Bray's equation applies also to non-aqueous solvents.

Another equation is proposed by Szyszkowski,[4] who concludes from his researches on partition coefficients[5] that the disturbing effect is due to undissociated molecules rather than ions. The fact that strong electrolytes, which are highly ionized, show the greatest deviations, rather suggests the opposite view, although the action of the molecules appears to be favored by recent investigators, whose arguments, it is true, are mostly applied at such high concentrations that the laws of solution break down *in toto*. Szyszkowski believes that ionization is not a spontaneous process, but is brought about by the absorption by the molecule of a critical increment of infra-red radiant energy. The same view is taken by Krüger,[1] who deduces from it the relation of Walden, that the ionizations in two different solvents are in the ratio of the cubes of the dielectric constants of the solvents.[2] This is in agreement with the view of Washburn and Strachan,[3] who speak of a "thermodynamic environment," modifying the thermodynamic properties of the solvent when ions are present. The partial pressure of any species in solution is then no longer given by Henry's law: $p_a = kx_a$, where x is the molar fraction, but by $p_a = f(c_i)x_a$, where $f(c_i)$ is some function of the ionic concentration. When these authors *assume* that $f(c_i)$ is of the form $k(1 + k'c_i^m)$, and thence "deduce" Kraus and Bray's equation, they appear to proceed in too arbitrary a fashion. Kraus and Bray's equation has no theoretical foundation.[4] Szyszkowski's final equation is

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[1] *J. Am. Chem. Soc.*, **34**, 855 (1912).

[2] *Ibid.*, **35**, 1315 (1913).

[3] *J. Am. Chem. Soc.*, **34**, 454 (1912); cf. Harkins, *ibid.*, **33**, 1836 (1911).

[4] *Medd. K. Vetensk. Nobel Inst.*, **3**, Nr. 2 (1914); **3**, Nr. 11 (1916); *Compt. rend.*, **157**, 767 (1913).

[5] *Ibid.*, **3**, Nrs. 3, 4 and 5 (1914).

$$\alpha^2/(1 - \alpha)V = K + k[(1 - \alpha)/V]^P = K + k\{[(1 - \alpha)/V]^{1/3}\}^p, \qquad (5)$$

which emphasizes that the non-ionized molecules are the cause of the deviations, and the dissociation function is assumed to be inversely related to the mean free path of these. The formula is applied to aqueous and non-aqueous solutions up to 0.5 *n*. The true dissociation constant *K* has approximately the value 0.01.[5] Table IX shows that the results for KCl can be very satisfactorily represented by the equation from about 0.1 *n*., without any alteration of conductivity values. It also applies to strong acids, and Kendall considers that the same holds good for his simpler equation.

The point of view adopted by Szyszkowski raises the important question of the supposed stimulating effect of ions or molecules on ionization. Arrhenius[6] suggested that the law of mass action may not apply to strong electrolytes: the "constant" *K* may be a function of the total ion concentration. This "salt action" is a maximum for a salt, and is greater for acids the greater the strength. Thus, $c_1^2/c_0 = f(c_1)$. This hypothesis of neutral salt action has been extended, on the basis of experiment, by Szyszkowski (*loc. cit.*), but has been very adversely criticized by McBain and Coleman,[7] who reject it. The

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[1] *Z. Elektrochem.*, **17**, 453 (1911).

[2] *Z. physik. Chem.*, **54**, 129 (1906). Kadlcova, *Chem. Listy*, **15**, 109 (1921).

[3] *J. Am. Chem. Soc.*, **35**, 681 (1913).

[4] Cf. Bates, *J. Am. Chem. Soc.*, **37**, 1421 (1915).

[5] Kraus, Electrically Conducting Systems, p. 69, states that Szyszkowski's equation does not apply generally to non-aqueous solvents.

[6] *Z. physik. Chem.*, **31**, 197 (1899), **31**, 197 (1899); **36**, 28 (1901); **37**, 490 (1901); Noyes and Abbot, *ibid.*, **16**, 125 (1895); van Laar, *ibid.*, **69**, 433 (1909).

[7] *J. Chem. Soc.*, **105**, 1517 (1914), with bibliography; Francis, Geake and Roche, *ibid.*, **107**, 1651 (1915); Harned. *J. Am. Chem. Soc.*, **37**, 2460 (1915), finds a real effect; McBain and Kam, *J. Chem. Soc.*, **115**, 1332 (1919).

TABLE IX

IONIZATION OF KCl AT 18° C. RECALCULATED BY SZYSZKOWSKI'S EQUATION; Λ/Λ_∞ FROM KOHLRAUSCH AND MALTBY

$$\Lambda_\infty = 129.91.$$

$$\frac{\alpha^2}{(1-\alpha)V} = 0.013 + 3.20\left\{\left(\frac{1-\alpha}{V}\right)^{1/3}\right\}^{1.26} = \phi.$$

V lit.	Λ	$\alpha = \Lambda/\Lambda_\infty$	$100\alpha^2/(1-\alpha)V$	100ϕ	Difference per cent
1.0	98.27	0.7565	235.0	178.1	− 56.9
2	102.41	0.7883	143.4	127.2	− 16.2
5	107.96	0.8310	81.5	78.4	− 3.1
10	112.03	0.8624	54.1	54.2	+ 0.1
20	115.75	0.8910	36.4	37.2	+ 0.8
50	119.96	0.9234	22.2	22.3	+ 0.1
100	122.43	0.9424	15.4	15.8	+ 0.4
200	124.41	0.9577	10.8	10.5	− 0.3
500	126.31	0.9723	6.81	6.51	− 0.30
1,000	127.34	0.9802	4.85	4.69	− 0.16
2,000	128.11	0.9862	3.52	3.48	− 0.04
5,000	128.77	0.9912	2.23	2.52	+ 0.29
10,000	129.07	0.9936	1.54	2.10	+ 0.56

evidence for or against an action of ions in increasing the electrolytic dissociation of a salt is very conflicting, and nothing certain can be asserted in this connexion.[1]

Empirical dilution laws were proposed by Rudolphi:[2]

$$\alpha^2/(1-\alpha)V^{1/2} = K, \qquad \text{or} \qquad c_i/c_0 = K$$

and van't Hoff:[3]

$$\alpha^{3/2}/(1-\alpha)V^{1/2} = K, \qquad \text{or} \qquad c_i^3/c_0^2 = K.$$

Kohlrausch[4] pointed out that van't Hoff's equation amounted to the statement: c_i/c_0 = *constant* × *mean distance between unionized molecules.* Vaubel[5] attempted to deduce van't Hoff's equation on the assumption of ionic hydration and polymerization of water to $(H_2O)_6$. Bousfield[1] assumes association of water, salt, and ions.

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[1] Poma and Tanzi, *Z. physik. Chem.*, **79**, 55 (1912); Walden, *Bull. Acad. Pétersb.*, 1055 (1912); Sachanov, *Z. physik. Chem.*, **87**, 441 (1914); Sachanov and Gontscharov, *J. Russ. Phys. Chem. Soc.*, **47**, 1244 (1915); Poma and Patroni, *Z. physik. Chem.*, **87**, 196 (1914); Palmaer and Melander, *Z. Elektrochem.*, **21**, 418 (1915); Kolthoff, *Chem. Weekblad*, **13**, 1150 (1916); Sachanov, *J. Russ. Phys. Chem. Soc.*, **48**, 361 (1916); Linde, *Z. Elektrochem.*, **29**, 163 (1923); Doumer, *Bull. Soc. Chim.*, **33**, 49 (1923); the balance of evidence speaks for an influence of ions.

[2] *Z. physik. Chem.*, **17**, 385 (1895).

[3] *Z. physik. Chem.*, **18**, 300 (1895); Hughes, *Phil. Mag.*, **42**, 134 (1921), deduces Rudolphi's and van't Hoff's equations; Jablczynski and Wisniewski, *Roczniki Chemji*, **1**, 116 (1921), deduce $c^{4/3}/c_0 = K$.

[4] *Z. physik. Chem.*, **18**, 662 (1895).

[5] *Z. angew. Chem.*, **15**, 395 (1902).

Storch[2] and Bancroft,[3] observing that Ostwald's and van't Hoff's equations are two limiting cases, proposed to cover all cases by the formula: $c_1{}^n/c_0 = K$, where n is a second constant. This applies very well to aqueous solutions even at high concentrations.

The important question as to whether the dilution law should contain a "true dissociation constant," i.e., whether it should go over into the Ostwald formula at infinite dilution, is now raised. The formulæ of van't Hoff and Storch do not fulfil this condition. Storch's equation may be written as:

$$\alpha^2/(1 - \alpha)V = k(\alpha/V)^{2-n};$$

it contains no true ionization constant; this is present in Kraus and Bray's equation, which is merely the above with the addition of K. In an important paper by Arrhenius,[4] in which a correction for the conductivity of the water was applied to Kohlrausch and Maltby's results, the conclusion was reached that at very high dilutions the electrolyte obeys Ostwald's dilution law, with a value of K, the true dissociation constant, of about 0.024. This occurs with KCl and $NaNO_3$ at dilutions of about 2.10^5 to 4.10^5 liters. The calculation of Arrhenius has been adversely criticized by Washburn,[5] but the results of Washburn and Weiland,[6] with ultra-pure water, appear to conform to Arrhenius's result. The experimental values, from smoothed curves, are as follows.

The smallest concentration used was 7.4945×10^{-6} mol./lit., and the next concentration used was 23.821×10^{-6} mol./lit., so that the results at lower concentrations are mere extrapolations.

The results have been criticized by Kraus,[7] who remarks that: "In order to establish the law of mass action as a consequence of experimental observations it must be shown that, over a measurable concentration interval, points on the curve [showing K as a function of c] necessarily lie on a horizontal straight line. As this has not been done, it is evident that Washburn's conclusion remains in doubt." It appears to the writer that this criticism is a little unfair. The region of concentration in which the law of mass action may be expected to apply at all is necessarily a very narrow one, in which experiment is extra-

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[1] *Z. physik. Chem.*, **53**, 266 (1905); *Proc. Roy. Soc.*, **74**, 563 (1905); *Phil. Trans.*, **206**, 101 (1906); *Trans. Farad. Soc.*, **15**, 47 (1919).

[2] *Z. physik. Chem.*, **19**, 13 (1896).

[3] *Z. physik. Chem.*, **31**, 188 (1899), cf Kohlrausch, *ibid.*, **18**, 662 (1895); *Beibl. Ann. Physik*, **25**, 54 (1901); Hughes, *Phil. Mag.*, **42**, 428 (1921), also deduced Partington's equation on the assumption of activity of ions; Georgevics, *Z. physik. Chem.*, **90**, 340 (1915).

[4] "Die Berechnung des elektrischen Leitungs-vermögens in sehr verdunnten wässrigen Lösungen," *Medd. K. Vetensk. Nobel Inst.*, **2**, Nr. 42 (1913); Faraday Lecture, *J. Chem Soc.*, **105**, 1414 (1914).

[5] *J. Am. Chem. Soc.*, **40**, 106 (1918).

[6] *J. Am. Chem. Soc.*, **40**, 146 (1918).

[7] Electrically Conducting Systems, p. 99.

TABLE X

CONDUCTANCE OF KCl

Temperature 18°. Mol. Wt. KCl = 74.560. Cell constant based on $\kappa = 0.01288$ ohm^{-1} for specific conductance at 25° of a solution of 7.43000 gm. KCl in 1000 gm. solution, weights in air. Conductance to 0.02 per cent.

$c \times 10^3$	$\kappa \times 10^6$	Λ	$\alpha = \Lambda/\Lambda_0$	$K = \alpha^2 c/(1 - \alpha)$
0.00	0.0	129.64	1.0	0.020 ± 0.001
0.02	2.5902_2	129.51_1	0.999_{01}	0.020_{02}
0.04	5.1753_6	129.38_4	0.998_{01}	0.020_{06}
*0.06	7.7554_9	129.25_8	0.997_{06}	0.020_{22}
0.08	10.330_9	129.13_8	0.996_{13}	0.020_{50}
0.10	12.902_9	129.02_9	0.9952_9	0.0210_2
*0.30	38.535_3	128.45_1	0.9908_3	0.0321_0
0.40	51.297_6	128.24_4	0.9892_3	0.0363_3
0.60	76.721_4	127.86_9	0.9863_4	0.0427_8
0.80	102.04_1	127.55_1	0.9838_9	0.0480_6
1.00	127.25_8	127.25_8	0.9816_3	0.0524_4

ordinarily difficult. The fact that even two experimental values were obtained in this region, or at any rate very near it in the case of the number 0.0321, is a great advance on anything which had been attempted before, and Washburn and Weiland's work still remains unique. The method of extrapolation used by Washburn has already been discussed (p. 530).

Bousfield[1] finds that van't Hoff's equation gives good results with KCl at dilutions from 200 to 2000 liters, and considers it justifiable to "extrapolate with great accuracy past the point where water impurities introduce errors, into the limiting region of infinite dilution." This leads to a limiting form of the equation when c is very small and α is nearly 1:

$$\Lambda_\infty - \Lambda = kc^{1/2}.$$

At very high dilutions the active mass of the undissociated portion is then proportional to the square root of the mass of the water. It appears, however, that the Ostwald formula is probably the right one at very high dilutions.

Many suggestions have been made to explain the deviations from the law of mass action shown by strong electrolytes.[2]

1. *Experimental Errors:* The suggestion that experimental errors, which become very large when $1 - \alpha$ is very small, cause more than a small part of the observed deviations[3] can hardly be entertained. Similar deviations are shown in alcoholic solutions,[4] in which the ionization is perceptibly less than in water, and in which the error in $1 - \alpha$ is much less.

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[1] *J. Chem. Soc.*, **103**, 307 (1913).

[2] Cf. Partington, *J. Chem. Soc.*, **97**, 1158 (1910); *Trans. Farad. Soc.*, **15**, 98 (1919); Sachanov, *Z. Elektrochem.*, **20**, 529 (1914).

[3] Ostwald, Grundriss der allgemein. Chem., 1899, 406; Rothmund and Drucker, *Z. physik. Chem.*, **46**, 827 (1903); *ibid.*, **49**, 563 (1904); Drucker, Die Anomalie der stärken Elektrolyte, *Ahrens' Sammlung*, **12** (1905).

[4] Völlmer, *Ann. Physik*, **52**, 328 (1894).

2. *Calculation of the Ionization:* The formula $\alpha = \Lambda/\Lambda_\infty$ can apply only when the ionic mobilities are independent of concentration.[1] In concentrated solutions this is certainly not the case, but the experimental values of the transport numbers given in a former section seem to support the assumption that, in fairly dilute solutions at least, the ratio of the mobilities may be regarded as constant. There is great diversity of opinion, however, on this matter.

3. *Complex Formation:* The possibility of the formation of ionic hydrates does not, in dilute solution, make any change in the form of the dilution law.[2] Complex ion formation would cause modification, but there is no evidence of the presence of such ions in solutions of salts such as KCl.[3] In such cases as $CuSO_4$ the formation of complex ions is by no means improbable.

4. *The Theory of Partial Dissociation is Incorrect:* Sutherland [4] suggested that the ionization of all ordinary electrolytes in solutions of all concentrations is complete. The differences of molecular conductivity at different dilutions are assumed to be due to the varying viscosity of the solution, and to two new types of viscosity of electrical origin. No quantitative theory was reached.

J. C. Ghosh [5] revived this theory, but instead of relying on new, purely hypothetical, viscosities, he assumes that all the ions are not in the same condition. A certain fraction exist in a state of perfect freedom, moving about like gas molecules, whilst another part includes ions which are fixed at definite points, in the same manner as the ions of a crystal arranged in a space lattice. Although the salt exists in solution wholly as ions, separated from one another by distances which increase with the dilution, and bound by electrostatic forces, only a fraction of these ions are free to move with translatory motion, these free ions being those which have kinetic energies greater than the limiting values equal to the potential energies of electrostatic attraction. The number of free ions is calculated by a formula based on Maxwell's formula for the distribution of energy among gas molecules.

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[1] F. Kohlrausch, *Ann Physik*, **50**, 388 (1893), H Jahn, *Z physik. Chem*, **27**, 354 (1898), **33**, 545 (1900); **35**, 8, **37**, 673 (1901), **58**, 641 (1907), Noyes and Kato, *Carnegie Inst. Washington Pub.*, No **63**, 326 (1907), Drucker and Krsnjavi, *Z. physik. Chem*, **62**, 731 (1908); Sackur, *Z. Elektrochem.*, **7**, 784 (1901), Goodwin and Haskell, *Z. physik. Chem.*, **52**, 630 (1905); Loeb and Nernst, *ibid.*, **2**, 956 (1888), Bein, *ibid*, **27**, 41 (1898), Noyes, *Technological Quarterly*, **17**, 295 (1904), Arrhenius, *Z physik Chem.*, **37**, 315 (1901), Abegg, Theorie der elektrolytische Dissociation, *Ahrens' Sammlung*, p. 232 (1903). See later under Lorenz's theory.

[2] Morgan and Kanolt, *Z. physik. Chem*, **48**, 365 (1904), Wegscheider, *ibid.*, **69**, 603, 609 (1909); Nernst, Theoretische Chemie, 8 10 Aufl, p. 611, Mie, *Ann. Physik*, **33**, 381 (1910); Müller and Romann, *Compt. rend.*, **156**, 1889 (1913), **157**, 400 (opposite view); Dhar, *Z. Elektrochem*, **20**, 57 (1914).

[3] Cf. Braley and Hall, *J. Am Chem. Soc*, **42**, 1770 (1920), Schneider and Braley, *ibid.*, **45**, 1121 (1923), who conclude that complex ions are formed in NaCl + KCl; Remy, *J. Chem. Soc. Abst.*, 310 (1915), Mines, *Kolloid Z.*, **14**, 168 (1914), Lorenz, *ibid.*, 322; Lungo, *Nuovo Cim.*, **16**, ii, 173 (1918), Abegg and Labendzinski, *Z. Elektrochem.*, **10**, 77 (1904); Biltz, *Z. physik. Chem.*, **40**, 185 (1902), Bruni, Pellini and Pegoraro, *Z. Elektrochem.*, **13**, 621 (1907).

[4] *Phil. Mag.*, **3**, 161 (1902); **9**, 781 (1905), **12**, 1 (1906); **14**, 1 (1907); **16**, 497 (1908); cf. Barmwater, *Z. physik. Chem*, **28**, 115 (1899).

[5] *J. Chem. Soc.*, **113**, 449, 627, 707, 790 (1918).

For a binary electrolyte having its ions arranged in a cubical (rock-salt) lattice Ghosh finds the equation:

$$ln \frac{\mu_\infty}{\mu_v} = \frac{1}{2RT} \cdot \frac{N_0 E^2 \sqrt[3]{2N_0}}{D \sqrt[3]{V}},$$

where N_0 = Avogadro's constant = 6.06×10^{23}; E = electronic charge = 4.7×10^{-10} E.S. units; R = gas constant = 8.315×10^7 c.g.s. units; T = absolute temperature; D = dielectric constant of solvent; V = dilution in cc.

This requires that all electrolytes of this type should have the same ionization at the same dilution, which is not the case.[1] Again, for a ternary electrolyte with ions arranged in a fluorspar lattice, Ghosh finds the formula:

$$ln \frac{\mu_\infty}{\mu_v} = \frac{1}{3RT} \cdot \frac{3N_0E^2 . 2 \sqrt[3]{2N_0}}{D . \sqrt{3} . \sqrt[3]{V}} .$$

In applying these formulæ Ghosh assumes that some electrolytes are binary in some solvents, but ternary in others. For example, NEt_4I is assumed binary in acetaldehyde, but ternary in formamide, whereas in the latter solvent, which has great ionizing power, we should not expect association of the solute. The choice of the state of the electrolyte is purely arbitrary.[2] For some electrolytes in non-aqueous solvents the formula does not apply at all satisfactorily.[3]

Ghosh's theory would require equal ionizations of an electrolyte in two different solvents when:

$$D_1 \sqrt[3]{V_1} = D_2 \sqrt[3]{V_2},$$

a relation found empirically by Walden.[4] This is, however, only a very rough approximation.[5]

Ghosh's theory, although received in some quarters with warm approval,[6] has been severely criticized, and may now be regarded as untenable in its original form. The disagreement with experiment, pointed out above, has been again emphasized by Kraus[7] and others.[8] The theoretical foundations have been attacked by Chapman and George,[1] Sand,[2] and Kendall.[3] The latter also pointed out that "the remarkable coincidence of calculated and observed values in many tables is due to far too frequent errors of calculation and transcription."

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[1] Partington, *Trans. Farad. Soc.*, **15**, 98 (1919). This is also implied in Milner's formula; see below.

[2] Partington, *loc. cit.;* cf. Meldrum and Turner, *J. Chem. Soc.*, **93**, 876 (1908); **97**, 1605 (1910).

[3] Partington, *loc. cit.*

[4] *Z. physik. Chem.*, **54**, 129 (1906); Kadlcová, *Chem. Listy*, **15**, 109 (1921).

[5] Partington, *loc. cit.*

[6] Sand, *Trans. Farad. Soc.*, **15**, 171 (1919); Nernst, Lehrbuch, 8-10 Aufl., p. 613 ff.

[7] *J. Am. Chem. Soc.*, **43**, 2514 (1921).

[8] Arrhenius, *Z. physik. Chem.*, **100**, 9 (1922); Kallmann, *ibid.*, **98**, 433 (1921); Prins, *Chem. Weekblad*, **20**, 237 (1923).

Ghosh [4] believes that his equations could be made to fit acids and bases in aqueous solutions by assuming Grotthus conduction as well as ionic transport.

The theory that electrolytes are completely ionized, and that differences in conductivity are due to changes in mobility, is adopted by MacInnes.[5]

S. R. Milner,[6] who admits that Sutherland's calculations are "based on several speculative hypotheses which are not always convincing," has attempted to extend this point of view, and his calculations, although very difficult, are the most thorough and interesting in this field. He believes that the degree of ionization cannot be calculated from either osmotic or conductivity data. Insuperable difficulties are said to stand in the way of correlating changes of conductivity with changes of ionization, and the former are to be correlated with the action of interionic electrostatic forces on mobility, after the manner of Sutherland. Ions of strong electrolytes are not associated into molecules, but pairs of oppositely charged ions which are *temporarily* in close proximity will behave in some cases as if they were actually bound together. The influence of electrostatic forces affects equally the osmotic and conductivity data. The assumption of the ideal gas law in the deduction of Ostwald's equation amounts to the hypothesis that the interionic forces fall off extremely rapidly with the distance, i.e., "chemical" forces are postulated, as contrasted with electrical forces obeying the inverse square law. In bringing in interionic forces this assumption, Milner believes, must be discarded. The inverse square law may not apply to ions, but on the assumption that it does, he investigates, by a most involved calculation, the effect on the osmotic pressure, and believes that the resulting effect is of the order observed, and that there are, therefore, no "chemical" forces at all. All the ions are free in the sense that there are none combined by chemical forces into molecules, but there are, of course, "temporary associations" of the kind just described. The effect of the water molecules is assumed not to be representable as that of a continuous medium of definite dielectric constant, but "each ion is surrounded by a number of polarized water molecules which tend to form chains linking together pairs of temporarily nearest oppositely charged ions. . . . The general effect would be to increase the attraction between an ion and the nearest one to it of unlike sign at the expense of the attraction of more distant ones, which latter might be negligible in consequence." An ion may be at the same time both free and combined. A distinction between weak and strong electrolytes can only be made by assuming that, in the former, chemical forces are present, and since only general agreement is obtained with strong electrolytes, "it is doubtful whether a pure electrical theory can account for all the details of individual strong electrolytes." Milner's theory is, therefore, of no immediate practical service. His view of particles which are at once free and combined also raises questions. Are we to suppose, for example, that the molecules of krypton are "combined" because they exert forces on one another, as they undoubtedly do, since krypton is not an ideal gas?

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[1] *Phil. Mag.*, **41**, 799 (1921).

[2] *Phil. Mag.*, **45**, 129, 281 (1923).

[3] *J. Am. Chem. Soc.*, **44**, 717 (1922).

[4] *J. Chem. Soc.*, **113**, 790 (1918); cf. Auerbach and Zeglin, *Z. physik. Chem.*, **103**, 178 (1922); Mund, *Bull. Soc. chim. Belge*, **32**, 156 (1923).

[5] *J. Am. Chem. Soc.*, **43**, 1217 (1921); **41**, 1086 (1919). Cf. Schellenberg, *Ann. Physik*, **47**, 81 (1915); Kjellin. *Archiv. Kem. Min. Geol.*, **4**, No. 7 (1911); Harkins, *Proc. Nat. Acad. Sci.*, **6**, 601 (1920); Phillipson, *Bull Acad. Roy. Belge*, **8**, 76 (1922).

[6] *Phil. Mag.*, **23**, 551 (1912); **25**, 742 (1913); **35**, 214, 333 (1918); *Trans. Farad. Soc.*, **15**, 148 (1919).

Bjerrum[1] also assumes strong electrolytes completely ionized, but, on account of electrostatic forces between ions, they exhibit decreasing osmotic pressure, conductivity, and reactivity with increase in concentration. These effects are expressed by means of three coefficients, and an approximate formula for the activity coefficient is derived.

Lorenz[2] points out that the assumption of complete ionization requires a new definition of transport number, viz.,

$$n = xu_0/(xu_0 + yv_0),$$

where x and y are separate mobility coefficients for kation and anion. Kohlrausch's formula $\Lambda = \alpha F(u + v)$ is then replaced by $\Lambda = F(xu_0 + yv_0)$, where u_0 and v_0 are limiting values approached at infinite dilution. The rate of change of mobility with concentration is different for different ions.

Lorenz's Theory: Lorenz[3] calculates from the Stokes-Einstein formula for the motion of a particle in a viscous medium the radii of ions, and compares them with the radii of atoms calculated from Reinganum's formula.[4] The two are in general agreement, except in the case of lithium, the ion of which is found more than double the size of the atom. The conclusion is reached that hydration is absent except in the case of lithium. Other values for the atomic radii[5] showed that the values of the ionic radii found from the Stokes-Einstein formula were in agreement in the case of univalent organic anions and kations, and bivalent kations. Bivalent anions have mobilities less than the calculated. The diameter of the hydrogen ion is 0.25, that of the hydroxide ion 0.33, and that of the cæsium ion 0.56 of that calculated. The diameters of ions which, on the grounds of migration experiments, are assumed to have medium hydration are found the same as those of the gas molecules. Those ions which are strongly hydrated have larger ions. The calculation was extended to complex salts,[6] polyvalent ions,[7] and inorganic anions.[8] In the latter case (simple salts) the relation no longer holds, the divergencies being in both directions. The formula used by Lorenz in calculating the radius of an ion from its mobility, l_k (in ohm^{-1}), is: $l_k = (1/r).8.954 \times 10^{-7}$ at 18° in water. With newer values of fundamental constants the constant is 9.371×10^{-7}.

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[1] *Z. Elektrochem.*, 24, 321 (1918); *Medd. K. Vetensk. Nobel Inst.*, 5, No. 16 (1919).

[2] *Z. anorg. Chem.*, 111, 55 (1920).

[3] *Z. physik. Chem.*, 73, 252 (1910); cf. Dhar, *Z. Elektrochem.*, 19, 748 (1913).

[4] Cf. Lindemann, *Trans. Farad. Soc.*, 15, 166 (1919).

[5] *Z. anorg. Chem.*, 94, 265 (1916).

[6] Lorenz and Posen, *Z. anorg. Chem.*, 95, 340 (1916); 96, 81 (1916).

[7] *Ibid.*, 96, 217 (1916).

[8] *Ibid.*, 96, 231 (1916); cf. Lorenz and Scheuermann, *ibid.*, 117, 140 (1921) (benzene nucleus).

Hertz's Theory:[1] Hertz deduced theoretically the equation $\mu_0 - \mu = f(c^{1/3})$, and by a suitable adjustment of coördinates the relation between μ and c may be represented by a single curve for all electrolytes. The equation has been tested by Lorenz,[2] who finds that the constants are not independent of the electrolyte but have specific values for each ion.

Born's Theory: A method of calculating the radii of ions has been proposed by Born,[3] and applied by Lorenz[4] to calculate the degree of hydration of ions. Born assumes that the Stokes-Einstein equation for the motion of spheres in a viscous medium applies even to small ions, any discrepancies being due to electrical interaction between ions and solvent molecules (cf. Sutherland's theory, above). The electrical viscosity increases as the ion becomes smaller, whilst the fluid viscosity decreases. The resistance passes through a minimum, and in this way the diminishing values of ionic conductivity with decreasing volume of the simpler ions is explained. Born's calculations made the radii of alkali metal and halogen ions rather less than 10^{-8} cm.[5] Born's theory has been criticized by Kraus,[6] who shows that in non-aqueous solvents the order of ionic conductances is not the same as that predicted by Born's theory. The ionic mobilities are supposed primarily determined by the diameter of the shell of solvent molecules surrounding them, as was postulated long before by Bousfield.

Modifications of the Law of Mass Action: The suggestion of Arrhenius, that ionization is affected by the presence of ions, which has already been discussed (p. 559), led to modification of the law of mass action. Some observers have rejected any such modifications; e.g., Noyes[7] concluded that the degree of ionization is not even approximately given by the law of mass action, and he used the empirical equation of Barmwater:[8]

$$1 - \alpha = k(c\alpha)^{1/3}.$$

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[1] *Ann. Physik*, **37**, 1(1912).

[2] *Z. anorg. Chem.*, **113**, 135 (1920), Lorenz and Neu, *ibid.*, **116**, 45 (1921); Lorenz and Michael, *ibid.*, **116**, 161 (1921), Lorenz and Ostwald, *ibid.*, **114**, 209 (1920).

[3] *Z. Physik*, **1**, 221 (1920), *Z. Elektrochem.*, **26**, 401 (1920).

[4] *Z. Elektrochem.*, **26**, 424 (1920); Lenard, Weick and Mayer, *Ann. Physik*, **61**, 665 (1920).

[5] Lungo, *Nuovo Cim.*, **16**, ii, 173 (1918), also applies Stokes's equation and deduces Walden's relation $\Lambda_0\eta$ = const., independent of temperature. The diameters of ions are smaller than those of molecules, $H^{\cdot}$ and OH'-ions are only half the molecular size, and these have less friction in water than other ions.

[6] Electrically Conducting Systems, p. 203. Cf. Dummer, *Z. anorg. Chem.*, **109**, 31 (1919).

[7] *Technol. Quarterly*, **17**, 298 (1904).

[8] *Z. physik. Chem.*, **28**, 115 (1899); **45**, 557 (1903), **56**, 225 (1906); Walden, *ibid.*, **94**, 374 (1920). Noyes has since used the equation $(c\alpha)^n/c(1 - \alpha) = K$, with n varying from 1.4 to 1.6 for aqueous solutions of different salts over wide ranges of temperature: *J. Am. Chem. Soc.*, **30**, 335 (1908); Hunt, *ibid.*, **33**, 795 (1911).

The ionization is supposed to be given by $\alpha = \Lambda/\Lambda_0$, since the E.M.F.'s of concentration cells, calculated on the assumption that α changed with c according to the above equation, agreed to within 1 per cent in the case of KCl and NaCl between concentrations of N/600 and N/20. The empirical equation gave equally good results with salts dissociating into 2, 3 or 4 ions, the concentration of unionized salt in all cases being proportional to the 3/2 power of the ion concentration.

The most comprehensive treatment of ionic equilibrium from the point of view of modification of the law of mass action is that put forward by Jahn[1] and a similar theory by Nernst.[2] Jahn allows, in the derivation of the mass law from thermodynamics, that there is mutual action between ions and molecules and solvent. Nernst also assumed action between neutral salt molecules. Jahn's equation is:

$$\frac{n_1{}^2}{N - n_1} e^{-aN/n + n_1(2a/n - b/n)} = \text{const.} = K,$$

in which N = no. of mols. of salt dissolved in n mols. of solvent; n_1 = kation mol. fraction; e = base of natural logarithms; a, b, K = constants. The constants a and b are functions of temperature, pressure and composition of solute and solvent.

Nernst's equation is:

$$\frac{c_1{}^2}{c_0} e^{2c_1(m_1 + m_{12} - m_{01}) + c_0(2m_{01} - m_0)} = \text{const.},$$

in which c_1, c_0 are concentrations of ions and salt, m_1, m_0 are coefficients of influence between ions and between neutral molecules, m_{01} is the coefficient of influence between ions and molecules, and m_{12} the coefficient of influence between the two kinds of ions. The coefficients are determined by trial.[3]

The equations derived from the point of view of "activity coefficients" are described in Chapter XII.

Conductivity and Chemical Constitution: A number of regularities have been pointed out in the relations between conductivity and chemical constitution. These include[4] comparisons between ionic mobilities and between ionization constants, K, of the Ostwald dilution law.

Bredig[5] found that the mobility of elementary ions is a periodic function of their atomic weights, and rises with atomic weight in each family of elements.

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[1] *Z. physik. Chem.*, **33**, 545 (1900); **35**, 1; **36**, 453 (1901); **37**, 490; **41**, 257 (1902); **38**, 125 (1901).

[2] *Z. physik. Chem.*, **38**, 487 (1901); cf. Planck, Thermodynamics, *tr. Ogg*, 225, 234 (1903); P. Henderson, *Z. physik. Chem.*, **59**, 118 (1907).

[3] Göbel, *Z. physik. Chem.*, **42**, 59 (1902); Hoffmann and Langbeck, *ibid.*, **51**, 385 (1905); Henderson, *ibid.*, **59**, 124 (1907); Szyszkowski, *ibid.*, **58**, 420 (1907); **63**, 421 (1908); Rothmund, *ibid.*, **69**, 523 (1909).

[4] Cf. Lehfeldt, Electrochemistry, London, 1908, p. 93 f. (by T. S. Moore); Ostwald, Lehrbuch, II, 1, 674 f.

[5] *Z. physik. Chem.*, 13, 191 (1894); cf. Lorenz and Posen, *Z. anorg. Chem.*, **96**, 217 (1916).

Analogous atoms, with atomic weights exceeding 35, have approximately equal mobilities. Thus, the mobilities at infinite dilution of $\frac{1}{2}Mg^{\cdot\cdot}$, $\frac{1}{2}Ca^{\cdot\cdot}$, $\frac{1}{2}Sr^{\cdot\cdot}$ and $\frac{1}{2}Ba^{\cdot\cdot}$, at 25°, are 62, 66, 67 and 68, respectively; those for $Li^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $Rb^{\cdot}$ and $Cs^{\cdot}$ are, respectively: 42.6, 52.6, 75.5, 78.6 and 78.8. Isomeric and metameric anions have the same mobility: the equivalent mobilities of ortho-, meta- and para-toluic, and phenylacetic acids are 32.0, 32.1, 31.7 and 31.9, respectively, phenylacetic acid being metameric with the other three isomeric acids. This rule does not hold for kations.

The greater the number of atoms in an ion the smaller the mobility (Bredig, *loc. cit.*), provided anions are compared with anions, and kations with kations. The rule holds less rigidly among kations. The mobility of an ion is reduced by substitution of H by halogen, NH_2, NO_2, and sometimes CH_3.

Inorganic acids differ from organic acids[1] in that they are strong electrolytes in aqueous solution (except H_2CO_3, H_2S, HCN) and do not obey Ostwald's dilution law. Little is known as to their constitution, but it appears that addition of oxygen or sulphur assists the formation of ions ($H_2S_4O_6$ is as strongly ionized as HCl).

Organic acids have been well studied.[2] The ionization constant *K* of fatty acids decreases as the series is ascended, but the substitution of successive CH_2 groups does not cause a constant decrease. Substitution of H by Cl, Br, and I causes a large increase of *K*, the magnitude decreasing in the order given. The substitution of a second atom of Cl has less effect than the first, and a third less than the second. The effect of replacing Cl by CN is still further to increase *K*, and this is supposed to indicate that the CN group in HCN (a very weak acid) is differently constituted from that in cyanacetic acid. Substitution by halogen in the α position produces a greater effect on ionization than in the β position. Similar results have been found in the substitution of H by OH in all acids, fatty and aromatic, except in the case of *p*-substitution in the benzene nucleus.

Unsaturated acids ionize more readily than the corresponding saturated acids; different isomers (e.g., crotonic and isocrotonic acids) have different ionizations.

The aromatic acids show much greater regularity than aliphatic. In the case of substitution in the nucleus, the groups CH_3, OH, NO_2, Cl increase *K*, the effect being greater in the ortho- than in the meta- and para-positions; NH_2 decreases *K*, the greatest effect being in the ortho- and the least in the meta-position. In the case of two substituents in the same acid, the actual ionization is less than the value calculated on the assumption that each behaves independently, although in the case of α-dibromopropionic acid the discrepancy is not large. The same holds in general for aromatic acids.

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[1] Effects of substitution in organic acids, summary by Wegscheider, *Monatsh.*, **23**, 287 (1902); Nernst, Lehrbuch, 8-10 Aufl., p. 583.

[2] Ostwald, *J. prakt. Chem.*, **31**, 433 (1885); *Z. physik. Chem.*, **3**, 170 (1889); Walker, *ibid.*, **4**, 319 (1889); Bethmann, *ibid.*, **5**, 385 (1890); Bader, *ibid.*, **6**, 289 (1890); Walden, *ibid.*, **8**, 433 (1891); Bredig, *ibid.*, **13**, 289 (1894); Jones, Lloyd and Wiesel, *J. Am. Chem. Soc.*, **38**, 121 (1916) (alcohol solutions).

The transition of acids from the benzene to the pyridine series is accompanied by decrease in the ionization constant.

In the case of dibasic acids[1] the first ionization constant, calculated from conductivity, is equal to the sum of two ionization constants, one for each carboxyl group, which are equal if the acid is symmetrical. Of two dibasic acids which are analogous, the one with a larger second ionization constant appears to have a smaller first ionization constant (Ostwald).

Conductivity measurements have played an important part in the elucidation of the constitution of pseudo-acids.[2]

Organic bases do not exhibit such regularities as acids;[3] secondary bases are usually stronger than primary or tertiary.

In the case of neutral salts, organic and inorganic, it may be asserted that they are in general highly ionized, even if they are of weak acids or bases, and approximately to the same extent at equal dilutions. Some salts, e.g., $HgCl_2$, $HgCy_2$, are only slightly ionized. By the application of the Ostwald-Bredig dilution rule (p. 527) it has been found that KH_2PO_4 and KH_2AsO_4 ionize as monobasic acids.[4]

Isohydric Solutions: Two solutions containing salts with a common ion are said to be *isohydric* when the concentration of that ion is the same in both solutions. The conductivity of a mixture of such solutions is the mean of the conductivities of the separate solutions.[5] Consider the first salt AB. The mass law gives

$$K_1 = (A^{\cdot})_1(B')/V_1(AB),$$

where $(A^{\cdot})$, (B'), etc., are the actual numbers of mols. contained in a volume V of solution. Similarly for the second salt AC:

$$K_2 = (A^{\cdot})_2(C')/V_2(AC).$$

In general $(A^{\cdot})_1$ is not equal to $(A^{\cdot})_2$, since the ionizations are unequal.

When the solutions are mixed the concentration of the common ion in the mixture is seen to be $((A^{\cdot})_1 + (A^{\cdot})_2)/(V_1 + V_2)$ and this will be in equilibrium with the ionization of the salt AB when the equation:

$$K_1 = (B')[(A^{\cdot})_1 + (A^{\cdot})_2]/(V_1 + V_2)(AB) = (B').(A^{\cdot})_1/V_1(AB)$$

is satisfied, and with the ionization of the salt AC when the equation:

$$K_2 = (C')[(A^{\cdot})_1 + (A^{\cdot})_2]/(V_1 + V_2)(AC) = (C').(A^{\cdot})_2/V_2(AC)$$

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[1] Cf. Meldrum, *J. Phys. Chem.*, **15**, 474 (1911).

[2] Hantzsch, *Ber.*, **32**, 575 (1899); Hantzsch and Kalb, *ibid.*, **32**, 3109 (1899).

[3] Summary: Bredig, *Z. physik. Chem.*, **13**, 289 (1894).

[4] Complex and double salts: see Jones and Mackay, *Am. Chem. J.*, **19**, 83 (1897); Archibald, *Trans. Nova Scotia Inst. Sci.*, **9**, 307 (1891); Morgan, *Z. physik. Chem.*, **17**, 513 (1895); Steele, *Phil. Trans.*, **198**, 105 (1902); Werner and Miolati, *Z. physik. Chem.*, **12**, 35 (1893); **14**, 506 (1894). Except at high dilutions, complex ions appear to exist in solutions of double salts.

[5] Arrhenius, *Ann. Physik*, **30**, 51 (1887); *Z. physik. Chem.*, **2**, 284 (1888); **5**, 1 (1890).

is satisfied. By division:

$$(A^{\cdot})_1/V_1 = (A^{\cdot})_2/V_2.$$

On mixing such solutions in any proportions no displacement of the dissociation occurs, and hence the conductivity of the mixture is the mean of that of the solutions, provided the concentrations of the common ion were equal in the separate solutions.[1] This holds even for solutions of strong electrolytes, which do not obey the law of mass action.[2]

The conductivity of mixtures of acids varies considerably with dilution.[2] Arrhenius[3] found that the ionization of a weak acid in presence of one of its salts is inversely proportional to the amount of salt present.

The case of solutions containing two binary electrolytes with no common ion is difficult to work out. Arrhenius (*loc. cit.*) showed that when a weak acid and several strong electrolytes exist in the same solution, the respective degrees of dissociation may be calculated as though the dissociated part of the particular electrolyte were a dissociated part of a salt of the weak acid.

Sherrill[4] finds, in particular cases, that if the concentrations of the separate ions in mixtures of salts with no common ion are calculated by the equation

$$[A] \times [B]/A_xB_y = K(\textstyle\sum i)^{2-n},$$

where $\sum i$ = *total* ion concentration, the results are accurate to 0.5 per cent at 0.2 *n.*, and 0.25 per cent at 0.1 *n*. The ion concentrations were determined by conductivity.

Mackay[5] tested the assumption of Arrhenius that in a solution containing two salts with a common ion, each salt has a degree of ionization equal to that which it would have when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixed solutions. In a solution containing ammonium sulphate and chloride in 0.2009 *n*. concentration, the partial conductivity of the chloride was 2 per cent larger than the calculated, and that of the sulphate 5.2 per cent larger. The partial conductivities were found from the transport number and conductivity. Bray and Hunt[6] found in mixtures of hydrogen and sodium chlorides that the observed conductivities in solutions 0.001 to 0.2 *n*. were always 1.6 per cent less than those calculated in 0.1 *n*. solutions of each substance, the difference diminishing as the concentration fell. It was suggested that the conductance of an ion may depend on its actual concentration rather than on the total ion concentration. The measured and calculated values agreed on this assumption and on the assumption that the ionizations of HCl and KCl are equal.[7]

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[1] Cf. Arrhenius, *Z. physik. Chem*., **31**, 218 (1899); Bray and Hunt, *J. Am. Chem. Soc.*, **33**, 781 (1911).

[2] Wakemann, *Z. physik. Chem.*, **15**, 159 (1894).

[3] *Z. physik. Chem.*, **5**, 1 (1890). Cf. Dorochevski and Fridman, *J. Russ. Phys. Chem. Soc.*, **47**, 1615 (1915); *Chem. Abs.*, **10**, 2822 (1916).

[4] *J. Am. Chem. Soc.*, **32**, 741 (1910).

[5] *J. Am. Chem. Soc.*, **33**, 308 (1911).

[6] *J. Am. Chem. Soc.*, **33**, 781 (1911).

[7] See also Andreeff and Saposhnikoff, *J. Russ. Phys. Chem. Soc.*, **44**, 895 (1912); *Chem. Abs.*, **6**, 2878 (1912); Drucker, Gifford, Gomes, Gusman and Kasansky, *Z. Elektrochem.*, **19**, 797 (1913); Thomas and Baldwin, *J. Am. Chem. Soc.*, **41**, 1981 (1919).

Bjerrum[1] finds that the mass law holds in dilute solutions of salts in presence of a large excess of a second salt.

Doroschevski and Dvorshantschik[2] investigated the conductivities of mixtures of aqueous solutions of sodium and potassium salts, and salts of alkaline earth metals. The isohydric principle was confirmed, when the formula of Barmwater[3] for the ionization was used. The results with sulphates and carbonates agreed with the formula $\kappa = A - a/v^{1/8}$, where v = dilution, and A and a are constants. The separate salts of the alkaline earth metals obey the formula $\kappa = A - a/v^{1/4}$, whilst KI solution agrees with the formula $\kappa = A - a/v^{1/3}$.

Kraus[4] finds that the isohydric principle when applied to mixtures of salts leads to

$$C_i^2/C_u = f(\sum C_1),$$

where $\sum C_i$ is the sum of the ion concentrations, including all ions.[5] As the concentration of the second electrolyte increases, the function,

$$P_i/C_u = \sum P_i,$$

where P_i is the ionic product, reduces in the limit to the same form as the function resulting from the isohydric principle. The values for conductivity for mixtures of NaCl and HCl agree better with the experimental values than those calculated from the isohydric principle, and the equation $P_i/C_u = f(\sum C_i)$ is less accurate than $P_i/C_u = \sum P_i$.[6]

Stearn[7] finds the conductivities of mixtures of salts (halides of K and Na; concentrations 0.1 – 4.0 *n.*; 25° C.) less than those calculated, and that they increase with total salt concentration, and with increase of the ratio Na/K in the mixture. They decreased with increase in the ratio Cl/I. Complex formation is suggested.

Hydrolysis: In virtue of its slight ionization, pure water is capable of acting either as a weak acid or as a weak base:

$$H_2O \rightleftharpoons H^{\cdot} + OH'.$$

On the assumption that the mass law holds we have:

$$K[H_2O] = [H^{\cdot}][OH'] = K_w,$$

since the active mass of the water is constant. K_w is called the *ionization*, or *dissociation, constant of water.* In pure water $[H^{\cdot}] = [OH'] = c$, and thus

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[1] *Medd. K. Vet. Nobel Inst.*, 5, No. 25 (1919); Brönsted, *K. Danske Vet. Math. fys. Medd.*, **3**, 1 (1920); *K. Vet. Nobel Inst.*, 5, No. 25 (1919); Brönsted and Pedersen, *Z. physik. Chem.*, **103**, 307 (1922).

[2] *J. Russ. Phys. Chem. Soc.*, **45**, 1174 (1913); *Chem. Abs.*, **8**, 288 (1914); **46**, 371, 419 (1914); *Chem. Abs.*, **8**, 2515 (1914).

[3] See above; *Z. physik. Chem.*, **28**, 115, 424 (1899).

[4] *J. Am. Chem. Soc.*, **43**, 2507 (1921).

[5] Arrhenius, *Z. physik. Chem.*, **31**, 218 (1899).

[6] Kraus, Electrically Conducting Systems, p. 222.

[7] *J. Am. Chem. Soc.*, **31**, 218 (1922).

$K_w = c^2$. The value of c, and therefore of K_w, has been found in several ways.[1]

(i) E.M.F. of the oxy-hydrogen cell (see Chapter XII).[2] This gave $K_w = 0.64 \times 10^{-14}$ at 19° and 1.42×10^{-14} at 25-26°. In pure water $[\mathrm{H}^{\cdot}] = [\mathrm{OH}'] = K_w^{1/2}$.

(ii) The conductivity of pure water. Kohlrausch and Heydweiller (see p. 521) found $\kappa = 0.0384 \times 10^{-6}$ at 18°, from which $K_w = 0.61 \times 10^{-14}$. For, $\kappa = n(u + v)$, where n = no. of ions, i.e., $0.0384 \times 10^{-6} = n(318 + 174)$ or $n^2 = [\mathrm{H}^{\cdot}] \times [\mathrm{OH}'] = K_w = 0.61 \times 10^{-14}$.

(iii) Hydrolysis of esters by $\mathrm{H}^{\cdot}$ and OH' ions. Wijs[3] by the hydrolysis of methyl acetate with pure water, using the results on the relative rates of hydrolysis with $\mathrm{H}^{\cdot}$ and OH' ions, found $K_w = 1.44 \times 10^{-14}$ at 25°.

(iv) Hydrolysis of salts; the theory is given below. By this method Arrhenius[4] calculated $K_w = 1.21 \times 10^{-14}$ at 25°.

(v) Mutarotation of dextrose in aqueous, acid, or alkaline solutions.[5]

(vi) Hydrogen potential of acid or alkaline solutions.[6]

The value of K_w increases very rapidly with rise of temperature.[7] The heat of ionization is expressed by the formula:

$$Q = 27857.5 - 48.5T,$$

and K_w is 0.116×10^{-14} at 0° C., 0.281×10^{-14} at 10° C., 58.2×10^{-14} at 100° C., and 525×10^{-14} at 200° C. Noyes, Kato and Sosman[8] found that the ionization of pure water increased very rapidly with temperature between 0° C. and 100° C., less rapidly between 100° C. and 218° C., passed through a maximum between 250° C. and 275° C., and then decreased.

Consider the ionization of a weak acid, to which the law of mass action may be applied:

$$K_a = [\mathrm{H}^{\cdot}][\mathrm{A}']/[\mathrm{HA}].$$

The value of $[\mathrm{H}^{\cdot}]$ will usually exceed the value for pure water, i.e., about 1×10^{-7}, but in the dilute solution the relation $K_w = [\mathrm{H}^{\cdot}][\mathrm{OH}']$ must always be satisfied, from which it follows that $[\mathrm{OH}']$ must be very much less than 10^{-7}. The electro-neutrality principle gives: $[\mathrm{H}^{\cdot}] = [\mathrm{OH}'] + [\mathrm{A}']$. Hence:

$$[\mathrm{H}^{\cdot}] = K_w/[\mathrm{H}^{\cdot}] + K_a[\mathrm{HA}]/[\mathrm{H}^{\cdot}];$$

$$\therefore \quad [\mathrm{H}^{\cdot}]^2 = K_w + K_a[\mathrm{HA}].$$

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[1] Nernst, Lehrbuch, 8-10 Aufl., p. 589, Beans and Oakes, *J. Am. Chem. Soc.*, **42**, 2116 (1920).

[2] Ostwald, *Z. physik. Chem.*, 11, 521 (1893); Arrhenius, *ibid.*, 805; Nernst, *ibid.*, **14**, 155 (1894); Lorenz and Böhi, *ibid.*, **66**, 733 (1909); Lewis, Brighton and Sebastian, *J. Am. Chem. Soc.*, **39**, 2245 (1917), find $K_w = 1.012.10^{-14}$ at 25° by calculation.

[3] *Z. physik. Chem.*, **12**, 514 (1893).

[4] *Z. physik. Chem.*, **11**, 805 (1893), cf. Bray, *J. Am. Chem. Soc.*, **32**, 932 (1910); Seyler and Lloyd, *J. Chem. Soc.*, **111**, 138 (1917).

[5] Hudson, *J. Am. Chem. Soc.*, **31**, 1136 (1909); not an accurate method.

[6] Frary and Nietz, *J. Am. Chem. Soc.*, **37**, 2263 (1915); $K_w = 1.76 \times 10^{-14}$ at 25°.

[7] Heydweiller, *Ann. Physik*, **28**, 503 (1909).

[8] *J. Am. Chem. Soc.*, **32**, 159 (1910).

This equation is exact; usually K_w is negligible in comparison with K_a, so that we have approximately:

$$K_a = [H^{\cdot}]^2/[HA].$$

A similar expression can be deduced for bases: $K_b = [OH']^2/[BOH]$.

When we have to deal with solutions of salts of weak acids and bases, then *hydrolysis* occurs, i.e., the salt is decomposed by water with production of free acid and base:

$$AB + H_2O \rightleftharpoons HA + BOH \rightleftharpoons H^{\cdot} + A' + B^{\cdot} + OH'.$$

The result is easily detected qualitatively, since salts are nearly always highly ionized, and the anion or kation of the salt will combine with $H^{\cdot}$ or OH' ions from the water to form nearly unionized acid or base, leaving an excess of OH' or $H^{\cdot}$ ions, respectively, in the solution, which give it an alkaline or acid reaction.

Three cases must be considered:

(i) *Salt of a strong acid and a weak base* (e.g., aniline hydrochloride):

$$AB + H_2O \rightleftharpoons HA + BOH \rightleftharpoons H^{\cdot} + A' + BOH,$$

the acid HA being largely, and the base BOH hardly at all, ionized.

$$[BOH][HA]/[AB][H_2O] = \text{constant},$$

or, since $[H_2O]$ is practically constant:

$$[BOH][HA]/[AB] = \text{base} \times \text{acid/salt} = K_h,$$

where K_h is the *hydrolysis constant.* K_h is defined in a way independent of the ionic theory. The decomposition of salts by water was studied by H. Rose in 1851.[1]

If the concentration of AB is 1 mol. in v liters, then, when equilibrium is attained, we have, if x is the degree of hydrolysis:

$$[HA] = x/v, \qquad [BOH] = x/v, \qquad \text{and} \qquad [AB] = (1 - x)/v,$$
$$K_w = [H^{\cdot}][OH']; \qquad \text{hence} \qquad [OH'] = K_w/[H^{\cdot}] = K_w v/x,$$

the acid HA being completely ionized, and giving a $H^{\cdot}$ concentration of x/v = acid concentration; the base is assumed non-ionized. (The presence of the ion $B^{\cdot}$ of the salt will drive back the ionization of the weak base.) If $K_b = [B^{\cdot}][OH']/[BOH]$, then:

$$K_b = \left(v\frac{K_w}{x} \cdot \frac{1 - x}{v}\right)\frac{v}{x} = \frac{K_w(1 - x)v}{x^2},$$

so that:

$$K_w/K_b = x^2/(1 - x)v.$$

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[1] *Ann. Physik*, **82**, 545 (1851).

The hydrolysis calculated from the equation $AB + H_2O = HA + BOH$ gives the constant:

$$K_h = [HA][BOH]/[AB] = \frac{x}{v}\cdot\frac{x}{v}\Big/\frac{1-x}{v} = x^2/(1-x)v.$$

Hence

$$K_w/K_b = K_h.$$

Also,

$$x = -\frac{vK_w}{2K_b} \pm \sqrt{\frac{v^2}{4}\left(\frac{K_w}{K_b}\right)^2 + \frac{vK_w}{K_b}}\,.$$

In many cases K_b is much larger than K_w, so that the ratio K_w/K_b is very small. The expression then reduces to:

$$x = \sqrt{vK_w/K_b} = \text{const.} \times \sqrt{v},$$

so that the hydrolysis of a salt of a weak base with a strong acid is proportional to the square root of the dilution, and is easily calculated from the values of K_w and K_b.[1]

(ii) *Salt of a strong base with a weak acid* (e g., KCN). By a calculation exactly similar to the above we find:

$$x = -\frac{vK_w}{2K_a} \pm \sqrt{\frac{v^2}{4}\left(\frac{K_w}{K_a}\right)^2 + v\frac{K_w}{K_a}}$$

or, approximately: $x = \sqrt{vK_w/K_a}$ = const. × $\sqrt{v}$.

(iii) *Salt of a weak acid and a weak base* (e g., aniline acetate). The reaction is $AB + H_2O \rightleftharpoons HA + BOH$, the acid and base being practically unionized. With the same notation as before we find (the salt being nearly completely ionized):

$$[AB] = (1-x)/v, \qquad [A'] = (1-x)/v = [B^{\cdot}].$$

Also $[HA] = x/v = [BOH]$. The following three relations hold good:

$$K_w = [H^{\cdot}][OH'],$$

$$K_a = [H^{\cdot}][A']/[HA] = [H^{\cdot}]\frac{1-x}{v}\Big/\frac{x}{v},$$

$$K_b = [B^{\cdot}][OH']/[BOH] = [OH']\frac{1-x}{v}\Big/\frac{x}{v},$$

from which follows:

$$K_aK_b = K_w[(1-x)/x]^2.$$

Thus:

$$(1-x)/x = K_a^{1/2}.K_b^{1/2}/K_w^{1/2} = \text{const.}$$

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[1] Cf. Noyes and Melcher, *Carnegie Inst. Pub.*, No. 63, p. 94; hydrolysis of salts of weak bases and strong acids increases with rise of temperature.

Hence x, the degree of hydrolysis, is independent of dilution. We have also:[1]

$$[\mathrm{H}^{\cdot}] = K_a x/(1 - x) = K_a K_w^{1/2}/K_a^{1/2}.K_b^{1/2} = \text{const.}$$

The methods used in determining degree of hydrolysis are as follows:

(i) *Measurement of the catalytic effect of the* H˙ *or* OH′ *ion*, e.g., in the hydrolysis of an ester or the rate of inversion of cane sugar.[2] The rate of hydrolysis of the ester is determined in presence of a strong acid (or base), and the velocity constant, k, compared with that found when hydrolysis of the ester occurs in presence of the salt.

(ii) *Distribution measurements:* The solution containing the salt is shaken with an immiscible solvent in which the free acid or free base is soluble. From the known distribution ratio, the concentration in the solution is easily calculated.

(iii) *Freezing point lowering.*[3]

(iv) *Conductivity:* Let κ be the observed specific conductivity of a solution of BA of concentration c. The apparent equivalent conductance is $\kappa/c = (1 - x)(\kappa/c)_v + x(\kappa/c)_{HA}$, where κ_v is the conductivity the salt would have possessed had no hydrolysis occurred and κ_{HA} is the conductivity of the acid, assumed strong. The base is assumed very weak, so that it does not enter the conductivity equation. Rewriting the above we get:

$$x = (\Lambda - \Lambda_v)/(\Lambda_{HA} - \Lambda_v).$$

Λ_{HA} is the equivalent conductance of the free acid at practically infinite dilution; Λ_v is found by Bredig's method,[4] which consists in arranging the constituents of the solution so that $\Lambda = \Lambda_v$, i.e., $x = 0$. This is attained by adding excess of the free (practically unionized) base until Λ is constant.[5]

(v) *From values of* K_w, K_a *and* K_b.

(vi) *Determination of* H˙ *concentration by concentration cell measurements.*

Hydrolysis may very appreciably affect the results of conductivity measurements with very dilute solutions, especially when the values of the ionization constants of the acid and base differ.[6]

When the hydrolysis of salts is followed by conductivity, the change sometimes occurs slowly. This has been attributed to scarcity of ions;[7] to hydrolysis in stages;[8] to hydrate isomerism (e.g., green and violet chromic chlorides); and to colloid formation,[1] since in the case of substances showing this slow hydrolysis the weak acid or weak base often tends to form colloidal solutions.

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[1] Tizard, *J. Chem. Soc.*, **97**, 2490 (1910); hydrolysis of salts occupying intermediate positions, see Rohden, *J. Chim. Phys.*, **13**, 261 (1915); Griffiths, *Trans. Farad. Soc.*, **17**, 525 (1922), has considered the situation in extremely dilute solutions, when the weak acid and base are appreciably ionized.

[2] Ley, *Z. physik. Chem.*, **30**, 193 (1899); Bredig and Fraenkel, *Z. Elektrochem.*, **11**, 525 (1905); Kellogg, *J. Am. Chem. Soc.*, **31**, 403, 886 (1909); Henderson and Kellogg, *ibid.*, **35**, 396 (1913) (neutral salt action).

[3] Göbel, *Z. physik. Chem.*, **89**, 49 (1914).

[4] See p. 527; *Z. physik. Chem.*, **13**, 191 (1894); Ikawa, *Mem. Coll. Sci. Eng. Kyoto*, **i**, 320 (1908).

[5] Cf. Gibbs, Williams and Galajikian, *Philippine J. Sci.*, **8**, 1 (1913); Noyes, Kato and Sosman, *J. Am. Chem. Soc.*, **32**, 159 (1910); Huff and Name, *Am. J. Sci.*, **45**, 103 (1918).

[6] Böttger, *Z. physik. Chem.*, **46**, 602, 604 (1903); Hägglund, *Arkiv. Kem. Min. Geol.*, **4**, No. 11, p. 1 (1911); Euler and Ugglas, *Z. physik. Chem.*, **68**, 498 (1909); Hägglund, *J. Chim. Phys.*, **10**, 207 (1912).

[7] Kovalevski, *Z. anorg. Chem.*, **23**, 1 (1900).

[8] Antony and Giglio, *Gazetta*, **25**, 1 (1895); Goodwin, *Z. physik. Chem.*, **21**, 1 (1896); Malfitano, *Ann. Chim. Phys.*, **25**, 159 (1912); Quartaroli, *Gazetta*, **45**, 139 (1915).

Amphoteric Electrolytes: Some substances on ionization give two ions simultaneously, one positive and the other negative, leaving a residual molecule with two equal and opposite charges. This residue is considered as an ion, although its net charge is zero:[2]

$$XMY \rightleftharpoons X^+ + {}^-M^+ + Y^-.$$

Such an ion is called an *amphoteric* ("Zwitter") *ion.* Examples are shown by glycine, *o*-aminobenzoic acid, and perhaps methyl orange:

$$\begin{aligned} \mathrm{NH_2CH_2COOH + H_2O} &\rightleftharpoons \mathrm{HO.NH_3.CH_2COOH} \\ &\rightleftharpoons \mathrm{OH' + \overset{+}{N}H_3CH_2CO\overset{-}{O} + H^{\cdot}}. \end{aligned}$$

Very little is known of such types of equilibrium, although they are perhaps more common than is usually supposed.[3]

Beveridge[4] considers that the degree of hydrolysis of amphoteric electrolytes as determined by conductivity methods differs from that found by catalytic measurements. Methods which depend on $H^{\cdot}$ concentration all agree among themselves, but indirect methods depending on conductivity, freezing point, etc., give different values.

Adams[5] has considered amphoteric electrolytes from the point of view of the relative strengths of the acidic and basic functions. If we consider the dibasic acid HAH and treat the two $H^{\cdot}$ ions independently, we have:

$$K_1 = [\mathrm{H^{\cdot}}][\mathrm{AH'}]/[\mathrm{HAH}]; \qquad K_2 = [\mathrm{H^{\cdot}}][\mathrm{HA'}]/[\mathrm{HAH}];$$
$$K_3 = [\mathrm{H^{\cdot}}][\mathrm{A''}]/[\mathrm{HA'}]; \qquad K_4 = [\mathrm{H^{\cdot}}][\mathrm{A''}]/[\mathrm{AH'}].$$

If we represent the first and second ionization constants of the acid by K' and K'', respectively, we have:

$$K' = K_1 + K_2; \qquad K'' = K_3K_4/(K_3 + K_4).$$

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[1] Wagner, *Monatsh.*, **34**, 95 (1913), disputed by Tian, *Compt rend*, **172**, 1179 (1921); *J. Chim. Phys.*, **19**, 190 (1921). On the hydrolysis of aluminates see Hantzsch, *Z. anorg. Chem.*, **75**, 371 (1912); **30**, 289; Mahin, Ingraham and Stewart, *J. Am. Chem. Soc.*, **35**, 30 (1913); severely criticized by Blum, *ibid.*, 1499, and Slade and Polack, *Trans. Farad. Soc.*, **10**, 150 (1914); cf. Noyes and Whitney, *Z. physik. Chem.*, **15**, 694 (1894). The reaction is:

$$\mathrm{Al(OH)_3 + OH' = Al(OH)_2O' + H_2O = Al(OH)_2OH + OH'};$$

the conductivity increases slowly at first (first stage), then rapidly (second stage), and then slowly (decreasing concentrations). See under "Amphoteric Electrolytes."

[2] Küster, *Z. anorg. Chem.*, **13**, 127 (1896); Winkelblech, *Z. physik. Chem.*, **36**, 546 (1901); Lunden, *Arkiv. Kem. Min. Geol.*, **2**, No. 18, 1 (1906); Robertson, *J. Phys. Chem.*, **10**, 524 (1906).

[3] Nernst, Lehrbuch, 8–10 Aufl., p. 440, he refers to carbon monoxide as $\overset{+}{\underset{-}{\mathrm{C}}} = \mathrm{O}$.

[4] *Proc. Roy. Soc. Edinb.*, **29**, 648 (1909).

[5] *J. Am. Chem. Soc.*, **38**, 1503 (1916).

Three cases arise: (*a*) the acid is symmetrical and the H atoms ionize independently: $K_1 = K_2 = K_3 = K_4 = K$ and $K' = 2K$; $K'' = \frac{1}{2}K$; (*b*) the acid is unsymmetrical but the H atoms ionize independently: $K_3 = K_1$; $K_4 = K_2$ and $K'' = K_1K_2/(K_1 + K_2)$; (*c*) the acid is unsymmetrical and the H atoms do not ionize independently. Then $K'/K'' > 4$. For a tribasic acid, $K'/K'' > 3$. For phenolphthalein and crystal violet, K'/K'' is nearly equal to 4. In the case of glycine K_a (the acidic constant) is 1.8×10^{-10} and K_b (the basic constant) is 2.8×10^{-12}, so that $K' = 3.7 \times 10^{-3}$ and $K'' = 1.8 \times 10^{-10}$. It is nearly as strong a base as methylamine and is a stronger acid than monochloracetic.

Michaelis[1] finds, if x is the proportion of unionized molecules of an amphoteric electrolyte, that:

$$x = 1/(1 + K_a/[\mathrm{H}^{\cdot}] + K_b/[\mathrm{OH}']),$$

where K_a and K_b are the acidic and basic dissociation constants, respectively. Substances for which $K_aK_b \overset{=}{>} 10^{-14}$ are not capable of existing; at this point complete dissociation occurs.

Substances such as lead and aluminium hydroxides are sometimes called amphoteric electrolytes, since they behave as acids towards strong bases and as bases towards strong acids. The dissociation of such substances is really hydrolytic in character, and has already been considered.

Solubility Product: The effect of one substance in influencing the solubility of another is fairly general. The solubility of non-electrolytes in the presence of electrolytes is generally depressed according to the equations:

$$S = S_0(1 + Ac) \text{ or more exactly } S = S_0e^{-Bc},$$

where c is the concentration of electrolyte, and A, B are constants.[2]

The effect is a specific property of the electrolyte, although the order of electrolytes as regards their effect on solubility is nearly the same for different solutes. The effect, sometimes known as "salting out," is not confined to electrolytes: the effect of sugar in reducing the solubility of hydrogen in water is greater than that of salts (Euler, *loc. cit.*).[3] In some cases addition of salt causes a marked increase in the solubility of a non-electrolyte, e.g., salts of aromatic acids in the case of ether and water (Thorin, *loc. cit.*). The solubility of salts is in general depressed, but not always, by addition of non-electrolytes, the solubility change being nearly, but not quite, a linear relation (Rothmund, *loc. cit.*).

The solubilities of electrolytes in presence of each other, especially when a common ion is present, is of more importance than the above cases.

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[1] *Biochem. Z.*, **33**, 182 (1911).

[2] Rothmund, *Z. Elektrochem.*, **7**, 675 (1901); *Z. physik. Chem.*, **69**, 523 (1909); Nernst, *ibid.*, **38**, 494 (1901); Findlay, *J. Chem. Soc.*, **97**, 536 (1910); **101**, 1459 (1912). Geffcken, *Z. physik. Chem.*, **49**, 257 (1909); Euler, *ibid.*, **49**, 303 (1904); Thorin, *ibid.*, **89**, 685 (1915).

[3] Cf. Armstrong, *Proc. Roy. Soc.*, **81**, 80 (1908).

Consider the equilibrium:

$$\mathrm{AgCl\ (solid)} \rightleftharpoons \mathrm{AgCl\ (satd.\ sol.)}.$$

If by any means the amount of dissolved salt is decreased, more solid will pass into solution to maintain saturation. The dissolved salt is ionized:

$$\mathrm{AgCl\ (solid)} \rightleftharpoons \mathrm{AgCl\ (dissolved)} \rightleftharpoons \mathrm{Ag}^{\cdot} + \mathrm{Cl}'.$$

If the law of mass action applies:

$$[\mathrm{Ag}^{\cdot}][\mathrm{Cl}']/[\mathrm{AgCl}] = K \qquad \text{or} \qquad [\mathrm{Ag}^{\cdot}][\mathrm{Cl}'] = K[\mathrm{AgCl}].$$

The term $K[\mathrm{AgCl}]$ is constant, since the solution is saturated at a given temperature. Hence: $[\mathrm{Ag}^{\cdot}][\mathrm{Cl}'] = \text{const.} = S$, where S is called the *solubility product* of silver chloride. It may be assumed that this relation holds good when the concentrations $[\mathrm{Ag}^{\cdot}]$ and $[\mathrm{Cl}']$ are not equal, and that solid AgCl is in equilibrium with a solution containing its ions when the *ionic product* $[\mathrm{Ag}^{\cdot}][\mathrm{Cl}']$ is equal to the solubility product. If the salt is completely ionized, which is very nearly the case with AgCl on account of the great dilution, then, if x is the solubility, $S = x^2$, since each ion concentration is equal to x.

If the ionic product exceeds S, solid salt will precipitate out of solution until the ionic product becomes equal to S. This is illustrated by the precipitation of NaCl from a saturated solution by HCl gas. The Cl' ion concentration is increased, so that the product $[\mathrm{Na}^{\cdot}][\mathrm{Cl}']$ now exceeds its value in the saturated solution of NaCl. The precipitation restores the value S of $[\mathrm{Na}^{\cdot}] \times [\mathrm{Cl}']$, but this is now the product of a large Cl' concentration with a small $\mathrm{Na}^{\cdot}$ concentration, the excess of Cl' ion being paired with the $\mathrm{H}^{\cdot}$ ions in the solution.

The quantitative aspect of the solubility product relation was first described by Nernst.[1] Consider a completely ionized binary electrolyte AB dissociated into the ions $A^{\cdot}$ and B'. Then $[A^{\cdot}][B'] = \text{const.} = L_0^2$, where L_0 is the solubility. Suppose now x mols. of a second completely ionized electrolyte with a common ion is added. The solubility of the first salt is reduced to L where $L(L + x) = L_0^2$. This equation holds only for complete ionization of both salts, a condition rarely met with in practice.

Let α_0 be the ionization of the first salt in saturated solution, before any of the second salt is added. Let α_2 be the ionization of the second added salt in the solution, and α_1 the ionization of the first salt when the second is added. The concentrations of the ions of the first salt are $L\alpha_1$ and $L\alpha_1 + x\alpha_2$, where x mols. of the second salt are added. The ionic product is $L\alpha_1(L\alpha_1 + x\alpha_2)$. Assuming this to be equal to the ionic product of the first substance alone in saturated solution, we have:

$$L\alpha_1(L\alpha_1 + x\alpha_2) = L_0^2\alpha_0^2.$$

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[1] *Z. physik. Chem.*, **4**, 372 (1889).

By solving this equation for L we find:

$$L = -\frac{x\alpha_2}{2\alpha_1} + \sqrt{\frac{x^2\alpha_2^2}{4\alpha_1^2} + \frac{L_0^2\alpha_0^2}{\alpha_1^2}}\,.$$

If $\alpha_1 = \alpha_2 = \alpha$, this reduces to:

$$L = -\frac{x}{2} + \sqrt{\frac{x^2}{4} + \frac{L_0^2\alpha_0^2}{\alpha^2}}\,.$$

These equations enable us to calculate the solubility of one salt in presence of a second salt with a common ion.

In estimating the ionizations the rule of Arrhenius[1] is frequently used: in a mixture of two salts with a common ion, each salt has a degree of ionization equal to that which it has when present alone in a solution in which its ions have a concentration equal to the concentration of the common ion in the mixture. This is not quite accurate; other rules have been discussed in preceding sections.

The experimental results in a few typical cases are represented by the curves in Figs. 18, 19 and 20.[2]

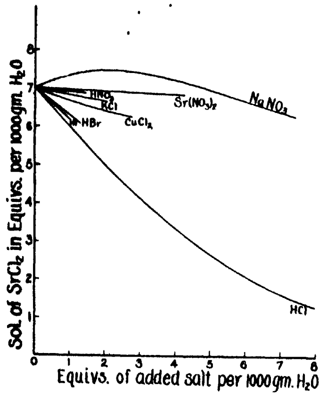

FIG. 18. Solubilities of Strontium Chloride in Presence of Other Salts

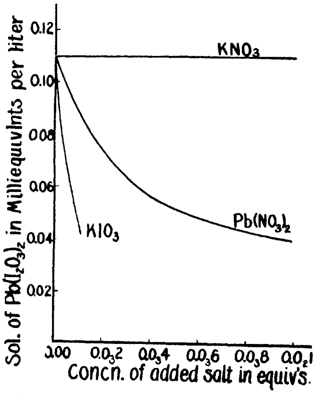

FIG. 19. Solubilities of Lead Iodate in Salt Solutions

In the case of $SrCl_2$ (Fig. 18) it is seen that the effect of substances without a common ion is not great. HCl causes the greatest effect, although HBr and HI, which have no common ion, also cause nearly as great a depression of solubility. $NaNO_3$, without a common ion, at first causes a slight increase in solubility, then a decrease.

The curves for $Pb(IO_3)_2$ are more in accordance with the theory as far as qualitative results go (Fig. 19).

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[1] *Z. physik. Chem.*, **2**, 284 (1888); **31**, 218 (1899).

[2] Kraus, Electrically Conducting Systems, pp. 271–272.

The curves in Fig. 20 relate to the solubilities of moderately strong organic acids in presence of HCl at 25°.[3] There is at first a rapid fall in solubility, as indicated by theory, then a nearly constant, slightly decreasing solubility, is reached on further addition of HCl.

All these results show that the simple theory of solubility product does not adequately represent the facts. The experiments of Nernst (*loc. cit.*) and of Noyes[1] showed better agreement. Noyes worked with silver bromate and nitrate, as well as with thallium salts, $TlNO_3$ with KNO_3, TlCNS with KCNS and $TlNO_3$. The silver salts gave satisfactory results, but the thallium salts did not conform to the theory. Noyes concluded that either the law of solubility product is incorrect, or else that conductivity measurements do not give a correct measure of the ionization. He then reversed the procedure and used solubility measurements to determine the degree of ionization.[2] In this way with $TlNO_3$, a strong electrolyte, he obtained values which agreed with Ostwald's dilution law. Kendall[3] has pointed out that this method may give erroneous results. Other experiments of Noyes[4] with tervalent chlorides also gave results in agreement with Ostwald's formula. The discrepancies were cleared up when Noyes found[5] that TlCl does not ionize to the same extent as alkali chlorides, as had previously been assumed. When this correction was made, the degrees of ionization found by solubility and conductivity methods were in agreement.

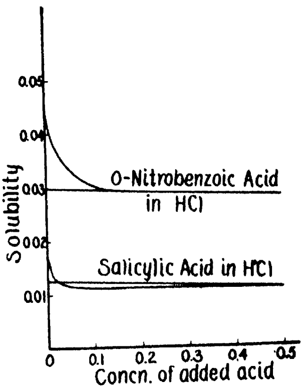

FIG. 20. Solubilities of Acids in Hydrochloric Acid Solutions

More recently the law of constancy of solubility product has been called in question.[6] Cameron found that the solubility of gypsum is increased by the addition of NaCl up to a certain point, but on further addition the solubility is depressed. Hill and Simmons found the same result with silver sulphate and nitric acid. Hill[7] pointed out that these results could only be explained on the assumption that the solubility products of gypsum and silver sulphate are not constant in presence of other electrolytes, and he proved that the same holds in the case of TlCl and Et_4NI, the product decreasing with increasing concentration of total electrolyte present.

Many other irregularities of this kind have been noticed. Thus Bray and Winninghoff[8] found the solubility of TlCl (in water) increased on addition of K_2SO_4 or KNO_3, but decreased in presence of KCl, $BaCl_2$ and Tl_2SO_4.

Kendall[3] experimented with slightly soluble organic acids (salicylic, *o*-nitrobenzoic), in presence of a second acid (picric, HCl) in aqueous solution at 25°. Real divergencies from constant solubility product were found. These were positive or negative according as the acids were chemically similar or dissimilar. The solubility of an acid in a solution of another acid is made up of two parts, one of which increases or decreases regularly according as the acid is more or less soluble in the aqueous second acid than in pure water, whilst the second part of the solubility decreases fairly rapidly according to the ionic strength of the solvent acid. All observed divergencies from constant solubility product can be satisfactorily explained by the first of these causes. Noyes' proposed method of determining ionization on the basis of the solubility method cannot therefore lead to accurate results.

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[1] *Z. physik. Chem.*, **6**, 241 (1890).

[2] *Z. physik. Chem.*, **6**, 259 (1890).

[3] *Proc. Roy. Soc.*, **85**, 200 (1911).

[4] *Z. physik. Chem.*, **9**, 603 (1892); Bray and Winninghoff, *J. Am. Chem. Soc.*, **33**, 1663 (1911).

[5] *Z. physik. Chem.*, **16**, 125 (1895); **26**, 152 (1898).

[6] Cameron, *J. Phys. Chem.*, **5**, 556 (1901); Hill and Simmons, *J. Am. Chem. Soc.*, **31**, 821 (1909); Brönsted, *J. Am. Chem. Soc.*, **42**, 761, 1148 (1920), *K. Danske Vidensk. Medd. Math. Phys.*, **2**, No. 10, 1 (1919); *J. Chem. Soc.*, **119**, 574 (1921).

[7] *J. Am. Chem. Soc.*, **32**, 1186 (1910).

[8] *J. Am. Chem. Soc.*, **33**, 1671 (1911).

Experiments of Hill[1] with $AgBrO_3$, TlCl and $PbCl_2$ in presence of varying amounts of acetic acid indicated that the solubility product decreases with increase in concentration of the more soluble electrolyte. Hill interprets his results as follows. Suppose the solution is saturated with AB and the added electrolyte is CD. The mixed solution contains the salts AB, CD, AD, and CB and the ions $A^{\cdot}$, B', $C^{\cdot}$, D'.[2] The solubility of $AB = L$ is then $[A^{\cdot}] + [AD] = [B'] + [CD]$, from which by multiplication we find $L = \sqrt{AB} + M$, where M has some positive value. It follows that if L becomes less than $\sqrt{AB}$ the solubility product is smaller than it would be in a saturated solution of AB in pure water. Hill's results show that this is the case, except in one instance, the solutility of Me_4NI in aqueous ammonia.

In the case of uni-bivalent salts such as $PbCl_2$, $Ca(OH)_2$, Ag_2SO_4, etc., Noyes and Bray[3] have shown that the solubility product principle breaks down completely. The product increases greatly in such cases, since the addition of the bivalent ion causes no great decrease in concentration of the univalent ion of the salt with which the solution is saturated. The conception of solubility product is "an approximate empirical principle" without theoretical foundation, according to Stieglitz;[4] it must be remembered, however, that the deduction rests upon the very improbable assumption that the solubility of a substance is not influenced by the presence of other substances unless these contain a common ion. All experimental evidence speaks against this. The failure can hardly be laid wholly at the door of the theory of electrolytic dissociation, or even of the law of mass action as applied to electrolytes.

Bray[5] has attempted to find a fresh theoretical basis for the law of solubility. The solubilities of ternary and higher types of salts have been investigated by Harkins,[6] but the results are not easily interpreted. Working with solutions of KCl, $Ba(BrO_3)_2$ and $PbCl_2$, he found:

(i) Addition of a salt of common univalent ion causes rapid decrease in solubility (in accordance with the solubility-product principle).

(ii) Addition of a salt containing a common bivalent ion causes:

- (*a*) Slight decrease and then increase in the solubility of the salt if the latter is moderately soluble;
- (*b*) Slight but continuous decrease in the solubility of less soluble salts (this was only confirmed to a concentration 0.2 n. of the added salt);
- (*c*) Continuous increase in solubility in the case of extremely soluble salts.

(iii) Addition of a salt with no common ion causes increase in solubility.

The interpretation of experimental results is somewhat uncertain because the ionization functions of each of the mixed electrolytes are unknown. In the cases of higher electrolytes especially, intermediate ions may exert an unknown effect and Harkins has shown that the solubility curves of these electrolytes may be qualitatively explained if the presence of such ions is assumed. Kendall and Andrews[7] measured the solubilities of acids of varying strength alone and in the presence of weak and strong acids up to high concentrations. The solubility of all acids is initially decreased by the addition of strong acids but, with few exceptions, passes through a minimum, whilst at high concentrations of added acid the solubility is markedly increased. The initial depression is assumed due to repression of ionization; it is greater the stronger the acid added, and is missing when the acid added is very weak. The minimum solubility is much lower than corresponds with the concentration of unionised molecules in pure water, perhaps on account of withdrawal of water to hydrate the added acid. The rise in solubility on further addition of strong acid is put down to complex formation.

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[1] *J. Am. Chem. Soc.*, **39**, 218 (1917).

[2] Complex ions might also be present.

[3] *J. Am. Chem. Soc.*, **33**, 1643 (1911); Noyes, Boggs, Farrell and Stewart, *ibid.*, p. 1650.

[4] *J. Am. Chem. Soc.*, **30**, 946 (1908); cf. Findlay, *Z. physik. Chem.*, **34**, 409 (1900).

[5] *J. Am. Chem. Soc.*, **33**, 1673 (1911).

[6] *J. Am. Chem. Soc.*, **33**, 1807 (1911); Harkins and Pearce, *ibid.*, **38**, 2679, 2709, 2714 (1916).

[7] *J. Am. Chem. Soc.*, **43**, 1545 (1921).

COMPLEX IONS[1]

Many methods are available for the detection and estimation of complex ions in solutions: purely chemical, migration data, partition coefficients, solubility measurements and application of Nernst's solubility product equation; electrode potentials, and cryoscopic measurements. Those methods which fall within the limits of this section have already been briefly considered.[2]

NON-AQUEOUS SOLUTIONS

Conductivities of Pure Liquids: The conductivities of pure liquids (including water) are very small, and are very largely influenced by the presence of small traces of impurities, so that their determination is a matter of considerable difficulty.[3]

In some cases, e.g., with sulphur dioxide, ammonia, ether and some hydrocarbons, the results resemble those obtained with gases, so that it has been assumed that these substances have no measurable conductance in the perfectly pure state. The existence of a limiting conductivity which is independent of the intensity does not prove that the liquid is perfectly pure. Carvallo (*loc. cit.*) showed that liquids containing known traces of impurities showed the effect. Previous electrical treatment usually influences the conductivity, methyl alcohol being an exception The prolonged passage of current leads to a conductivity limit, which may be greater or less than the true conductivity (Carvallo).

The measurements of Jaffé,[4] made with very pure liquids, showed that, in the case of hexane, the conductivity had a limiting value which was independent of temperature but depended on the nature of the containing vessel. Above 200 volts/cm. the current was independent of the potential gradient, and the results indicated a conductivity due to ionization by radiations from the vessel, as with gases. Part of the ionization was due to external radiation, since the conductivity decreased when the vessel was surrounded by lead screens. The conductivity of hexane when exposed to rays from radium[1] did not agree with the results of Thomson with gases. The specific velocities of the positive and negative ions were 6.03×10^{-4} and 4.17×10^{-4} cm./sec., respectively, and the coefficients of diffusion 1.50×10^{-5} and 1.03×10^{-5}. Van der Bijl,[2] by a method eliminating ionic diffusion, showed that, in the case of hexane, carbon tetrachloride and carbon disulphide, Thomson's formula:

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[1] See Complex Ions, A. Jaques, London, 1914.
Pick, *Diss.*, *Breslau*, 1906,

[2] See for examples: Sherill, *Z. physik. Chem.*, **43**, 705 (1903), Pick, *Diss.*, *Breslau*, 1908, Roloff, *Z. physik. Chem.*, *Z. anorg. Chem.*, **51**, 1 (1906), W. K. Lewis, *Diss.*, *Breslau*, 1908, Roloff, *Z. physik. Chem.*, **13**, 341 (1894); Jakowkin, *ibid.*, **13**, 539 (1894); **18**, 585 (1895); Plotnikov and Rokotjan, *J. Russ. Phys. Chem. Soc.*, **47**, 723 (1915), Leslie, *J. Chem. Soc.*, **99**, 1601 (1911); Jaques, Complex Ions, 1914; see also under the respective metals in Abegg's Anorganische Chemie.

[3] Walden, *Z. physik. Chem.*, **46**, 103 (1903); Carvallo, *Compt. rend.*, **151**, 717 (1910); **155**, 1609 (1912); **153**, 1144 (1911), **156**, 1755 (1913); *Ann. Physique*, **1**, 171 (1914); **2**, 142 (1914); Fassbinder, *Ann. Phys.*, **48**, 449 (1915) (considers previous measurements all affected by impurities); Schröder, *ibid.*, **29**, 125 (1909) (physical condition of electrodes affects results); Kraus, Properties of Electrically Conducting Systems, 1922; Walden, Elektrochemie nichtwässriger Lösungen, 1924 (full bibliography).

[4] *Ann. Physik*, **28**, 326 (1909).

$$du/dt = -an^2$$

is obeyed, n being the number of positive or negative ions per cc. and a the coefficient of combination.[3] It appears, on the whole, as if the conductivities of pure liquids, other than water or ionizing liquids, and of gases are similar in the mechanism by which the current is carried. As an example of the difficulties met with in this field, reference may be made to the decomposition of liquid sulphur dioxide by light, with formation of products which dissolve and increase the conductivity:[4]

$$3SO_2 = S + 2SO_3.$$

The values of the specific conductance, κ, for some pure liquids are given in the table opposite.

Ionizing Power of Solvents: Dutoit and Aston[5] considered that only associated solvents were capable of ionizing dissolved electrolytes, but the results of Walden[6] show that all liquids are capable of causing ionization to some extent.

One property of the solvent which has a marked influence on its ionizing power is the dielectric constant. This is considered in a later section, but it may be noted that the mass action constant K decreases rapidly with D, especially when D is less than 10.

The effect of association has also been studied by Turner,[7] who states that all associated liquids are conductors, and the best conductors are those which are most associated. A notable exception is water, and it is doubtful if this rule is general. The constitution of the solvent plays a part; acids in some solvents (e.g., water, alcohols) appear to form complexes with the solvent which are active in carrying the current, solutions in other solvents (e.g., nitrobenzene) having very low conductivities.[8] The chief factor governing the

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[1] Jaffé, *Ann. Physik*, **32**, 148 (1910); cf. Curie, *Compt. rend.*, **134**, 420 (1902).

[2] *Ann. Physik*, **39**, 170 (1912); Bialobjeski, *Le Radium*, **8**, 293 (1911).

[3] Conduction of Electricity through Gases, Cambridge, 1906, pp. 16, 17.

[4] Coehn and Becker, *Z. physik. Chem.*, **70**, 88 (1910).

[5] *Compt. rend.*, **125**, 240 (1897).

[6] *Z. physik. Chem.*, **54**, 129 (1906).

[7] *J. Chem. Soc.*, **99**, 880 (1911); Molecular Association, London, 1915.

[8] Kendall and Gross, *J. Am. Chem. Soc.*, **43**, 1426 (1921).

TABLE XI

SPECIFIC CONDUCTANCE OF PURE LIQUIDS

Liquid	Temperature ° C.	κ	Observer
SO_2	15	1.8×10^{-11}	Carvallo, *Ann. Physique*, **1**, 171 (1914); **2**, 142 (1914).
NH_3	15	3.8×10^{-10}	do.
NH_3	− 80	4.9×10^{-10}	do.
$(C_2H_5)_2O$	16	7.6×10^{-16}	do.
$(CH_3)_2CO$	15	1.2×10^{-10}	do.
CH_3OH	0–20	8.0×10^{-7}	do.
HCN	0	1.1×10^{-7}	do.
C_2H_5OH	17	1.2×10^{-9}	Carvallo, *Compt. rend.*, **156**, 1755 (1913).
$(C_2H_5)_2O$	—	1.3×10^{-13}	Fassbinder, *Ann. Physik*, **48**, 449 (1915)
C_2H_5OH	—	1.35×10^{-9}	Danner and Hildebrand, *J. Am. Chem. Soc.*, **44**, 2824 (1922).
C_6H_6 ...	—	$10^{-14} - 10^{-15}$	Holde, *Ber.*, **47**, 3239 (1914).
C_3H_7OH	18	1.7×10^{-7}	Kraus and Bishop, *J. Am. Chem. Soc.*, **43**, 1568 (1921).
$C_5H_{11}OH$	—	1.4×10^{-9}	Kraus and Bishop, *J. Am. Chem. Soc.*, **44**, 2206 (1922).
$N(CH_3)_3$. .	− 33.5	2.2×10^{-10}	Elsey, *J. Am. Chem. Soc*, **42**, 2454 (1920)
$(C_2H_5)_2NH$ ...	− 33.5	2.2×10^{-10}	do.
$C_2H_5NH_2$.	− 33.4	4.6×10^{-8}	do
$H.CO\,NH_2$ ..	25	2.8×10^{-6}	Davis, Putnam and Jones, *J. Franklin Inst.*, **180**, 567 (1915).
Ethyl acetate	25	less than 1×10^{-9}	Kendall and Gross, *J. Am. Chem. Soc*, **43**, 1426 (1921)
Ethyl benzoate	25	less than 1×10^{-9}	do.
Benzyl benzoate	25	less than 1×10^{-9}	do.
Acetone . ..	25	5.8×10^{-8}	do.
Acetophenone .	25	5.5×10^{-8}	do.
Acetic acid ...	25	2.4×10^{-8}	do
Propionic acid .	25	less than 1×10^{-9}	do
$CH_2ClCOOH$ ...	60	1.4×10^{-6}	do.
CCl_3COOH	60	6.2×10^{-9}	do.

ionizing power of solvents of low dielectric constant is the chemical nature.[1] A close relation between conductivity and specific refraction has been pointed out.[2] This is not remarkable in view of the well-known relation between refraction and dielectric constant.

Determination of Conductance: The general methods used for non-aqueous solutions are the same as those previously described for aqueous solutions. In general, however, much more care is needed to obtain reliable results with non-aqueous solutions than is required with aqueous solutions when the same degree of accuracy is sought. One of the main sources of error is chemical change of the solvent. Thus, alcoholic solutions readily undergo oxidation in contact with platinized electrodes, and the conductance steadily decreases if this is not avoided.[1]

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[1] Sachanoff, *J. Russ. Phys. Chem. Soc*, **43**, 526 (1911), *C. A.*, **6**, 179 (1912); Plotnikoff, *Chem. Soc. Abs.*, **114**, (ii), 183 (1918).

[2] Getman and Gibbons, *J. Am. Chem. Soc.*, **37**, 1990 (1915), Walden, *Z. physik. Chem.*, **59**, 385 (1907).

The design of conductivity cells has been considered by Morgan and Lammert, on the basis of Washburn's investigations (see p. 517). They have pointed out the modifications required with non-aqueous solutions.[2] The most suitable standard liquid for the determination of the cell constant was found to be standard potassium chloride solution diluted with 95 per cent alcohol instead of water, the solution being forced into the cell by purified air. The usual methods of cleaning and drying the electrodes are inapplicable. A method is described in which the electrodes are kept short-circuited, and the two electrodes should have as nearly as possible the same contact potential when immersed in the solution. When the electrodes are properly cleaned no change of conductivity occurs with change of P.D. Fig. 21 shows a cell designed by Morgan and Lammert (*loc. cit.*) for non-aqueous solutions.[3]

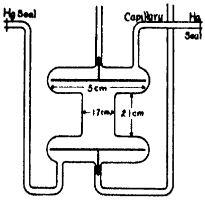

FIG. 21. Conductivity Cell for Non-Aqueous Solutions

Investigations on Non-Aqueous Solutions:[4] The investigations on non-aqueous solutions are of very unequal merit. Some are very inaccurate, and before using any data in this field a very careful comparison is required. Of the earlier results, those of Völlmer[5] may be mentioned as reliable.

The simple relations between conductance and concentration found with aqueous solutions do not, in general, appear when other solvents are used. In some cases, when the dielectric constant is high, the conductance (molar or equivalent) decreases with increasing concentration as in the case of aqueous solutions. This is found with solutions in liquid ammonia and methylamine. In other cases, when the dielectric constant is fairly low (not greater than 20), a minimum conductance is attained. When the dielectric constant is about 20, the conductance decreases with increasing concentration at low concentrations and becomes constant at higher concentrations. When the solvent has a very low dielectric constant, the conductance increases with the concentration. In all cases, above concentrations of 1 molar, the conductance appears to decrease with increasing concentration.[6]

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[1] Partington, *J. Chem. Soc.*, **99**, 1938 (1911).

[2] *J. Am. Chem. Soc.*, **45**, 1692 (1923).

[3] Cf. Robertson and Acree, *J. Phys. Chem.*, **19**, 381 (1915); for ordinary work Partington (*loc. cit.*) found the stoppered type of cell, Fig. 2, p. 516, most suitable. The cell is nearly completely filled, and air and moisture excluded by a good stopper covered with Faraday's cement.

[4] Cf. Müller, *Ahrens. Sammlung*, **27**, 268 (1923).

[5] *Ann. Physik*, **52**, 328 (1894).

[6] Anderson, *J. Phys. Chem.*, **19**, 753 (1915); Mathews and Johnson, *ibid.*, **21**, 294 (1917); Isbekoff and Plotnikoff, *Z. anorg. Chem.*, **71**, 328 (1911); Sachanoff, *Z. physik. Chem.*, **83**,

Steele, McIntosh and Archibald[1] attempted to explain the abnormal results on the assumption of complex formation between solute and solvent, on the basis of which they arrived at the relation

$$\kappa V^n = \alpha K,$$

where κ = specific conductance, α = degree of ionization, V = dilution, K = constant, and n = number of mols. of solute entering into combination. This work has been very severely criticized by Plotnikoff,[2] who shows that it is incapable of covering some known results.

Walden[3] considers that the position of the minimum molar conductance is related to the dielectric constant D of the solvent according to the expression $DV^{1/3}$ = const., for a given electrolyte, where V is the dilution corresponding with the minimum molar conductance (corrected for viscosity).

Creighton and Way state that the value of Λ_∞ is greater in aliphatic than in aromatic solvents of the same type.[4] In the case of p-tolyltrimethylammonium iodide the value of Λ_∞ in different solvents is greatest when the latter contain a $-$CHO group, and least when they contain a $-$COOH group.

In the case of alcohols[5] the results are more or less similar to those with water; methyl alcohol shows the closest similarity, and the divergence increases with the complexity of the alkyl group. The ionization is smaller than in water,[6] and conductance usually increases with dilution. Similar results have been obtained with solutions in phenol,[7] which is of the water type.

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129 (1913); Sachanoff, *J. Russ. Phys. Chem. Soc*, **44**, 321 (1912); *C. A*, **6**, 1564 (1912); Getman and Gibbons, *J. Am. Chem. Soc.*, **36**, 1630 (1914), **37**, 1990 (1915).

[1] Steele and McIntosh, *Proc. Roy. Soc.*, **74**, 321 (1905); Archibald, *J. Am. Chem. Soc.*, **29**, 665 (1907).

[2] *J. Russ. Phys. Chem. Soc*, **40**, 1243 (1908), *Chem. Soc. Abs*, **96**, (ii), 13 (1909); Franklin and Gibbs, *J. Am. Chem. Soc.*, **29**, 1389 (1907), see, however, Sachanoff, *J. Russ. Phys. Chem. Soc.*, **43**, 534 (1911); *C. A.*, **6**, 180 (1912)

[3] *Bull. Acad. Sci. Petersburg*, **7**, 1083 (1913), Sachanoff and Prsheborovski, *J. Russ. Phys. Chem. Soc.*, **47**, 849 (1915), Sachanoff and Rabinovitsch, *ibid*, p. 859, *C. A.*, **9**, 3000 (1915).

[4] *J. Franklin Inst.*, **186**, 675 (1918).

[5] Cattaneo, *R. Acad. Torino*, **28**, 617 (1893), Vollmer, *Ann. Physik*, **52**, 328 (1894), Partington, *J. Chem. Soc.*. **99**, 1937 (1911); *Trans. Farad. Soc.*, **15**, 111 (1919); Robertson and Acree, *Eighth Internat. Congress Appl. Chem*, **26**, 609 (1912), *J. Phys. Chem*, **19**, 381 (1915); Goldschmidt and coworkers, *Z. physik Chem*, **89**, 129 (1915), **91**, 46 (1916); *Z. Elektrochem.*, **20**, 473 (1914); Getman and Gibbons, *J. Am. Chem. Soc.*, **37**, 1990 (1915); Kreider and Jones, *Am. Chem. J.*, **45**, 282 (1911), **46**, 574 (1911), and numerous papers by Jones in later issues; Turner, *J. Am Chem. Soc*, **40**, 558 (1908); Lloyd and Pardee, *Carnegie Inst. Pub.*, **260**, 99 (1918); Dutoit and Rappeport, *J. Chim. Phys.*, **6**, 545 (1908), Archibald and Patrick, *J. Am. Chem. Soc.*, **34**, 369 (1912), methyl alcohol: Völlmer, *loc. cit.;* Kreider and Jones, *loc. cit.;* Goldschmidt and Thuesen, *Z. physik. Chem.*, **81**, 30 (1913); Rimbach and Weitzel, *Z. physik. Chem.*, **79**, 279 (1912), cf. Partington and Grant, *Trans. Farad. Soc.*, **19**, 414 (1923).

[6] Keyes and Winninghoff, *J. Am. Chem. Soc.*, **38**, 1178 (1916), Bishop and Kraus, *ibid.*, **43**, 1568 (1921); **44**, 2206 (1922). Acetone: Walden, *Z. physik. Chem.*, **54**, 208 (1906); Dutoit and Levier, *J. Chim. Phys*, **3**, 435 (1905); Roshdestwensky and Lewis, *J. Chem. Soc.*, **99**, 2138 (1911).

[7] Kraus and Kurtz, *J. Am. Chem. Soc.*, **44**, 2464 (1922).

Numerous measurements in anhydrous formic acid have been made. The electrolysis of sodium formate in formic acid yields carbon monoxide.[1] The conductances have been determined by Schlesinger and co-workers.[2] Higher fatty acids have also been used. The conductance in acetic acid[3] decreases with dilution, the effect being more rapid with propionic acid. The effects are very marked with concentrated solutions, and complex formation is indicated.[4]

Amines have been investigated by Sachanoff,[5] who found that the conductances in aniline, methylaniline, and dimethylaniline decrease in the order given. Dimethylaniline is on the border between ionizing and non-ionizing solvents. Aliphatic amines[6] and pyridine[7] have been investigated. In nitrobenzene solutions halogens are non-conductors[8] whilst ICl_3, IBr give conducting solutions, electrolysis of which takes place according to Faraday's law.[9]

A very interesting solvent is formamide, $H.CO.NH_2$, which forms good conducting solutions, although less so than water. The physical properties of the two solvents are very similar. In some cases the results are different, e.g., CBr_3COOH is highly ionized in water but only slightly so in formamide.[10]

An extensive series of measurements have been made in anhydrous ammonia.[11] The solutions behave similarly to aqueous solutions in that the conductance increases with dilution and attains a limiting value.[12] The conductance of a salt in ammonia is, in general, higher than that in water, although the ionization is less. Ammonia approaches alcohol and acetone in ionizing power. In some cases (e.g., KNH_2, $HgCy_2$ and AgCN) a minimum conductance is observed. Franklin[13] found in the case of $Cu(NO_3)_2$, $Zn(NO_3)_2$, $KHgCy_2$ and KNH_2 two maxima and a minimum. Solutions of alkali metals in ammonia at the boiling point (– 33.5°) conduct ionically, the negative ions being free electrons.[1] Concentrated solutions exhibit metallic conductance, and at the highest concentrations resemble alloys. The value of κ for saturated solutions of K and Na is of the same order as that for metallic iron.[2] On dilution, the conductivity falls rapidly.

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[1] Hopfgartner, *Monatsh.*, **32**, 523 (1911).

[2] *J. Am. Chem. Soc.*, **36**, 1589 (1914); **38**, 271 (1916); **41**, 72, 1921 (1919).

[3] Sachanoff, *J. Russ. Phys. Chem. Soc.*, **43**, 526 (1911).

[4] Sachanoff, *J. Russ. Phys. Chem. Soc.*, **43**, 534 (1911); *C. A.*, **6**, 180 (1912); Hopfgartner, *Monatsh.*, **33**, 123 (1912); **34**, 1313 (1913); Konovaloff, *J. Russ. Phys. Chem. Soc.*, **24**, 440 (1893); *Chem. Soc. Abs.*, **64**, (ii), 356 (1893).

[5] *J. Russ. Phys. Chem. Soc.*, **42**, 683 (1910); *C. A.*, **5**, 3749 (1911); **44**, 324 (1912); *C. A.*, **45**, 102 (1913); *C. A.*, **7**, 1831 (1913); *Z. physik. Chem.*, **85**, 129 (1913).

[6] Fitzgerald, *J. Phys. Chem.*, **16**, 621 (1912).

[7] Baskov, *J. Russ. Phys. Chem. Soc.*, **46**, 1699 (1914); *C. A.*, **9**, 2171 (1915); Anderson, *J. Phys. Chem.*, **19**, 753 (1915); Mathews and Johnson, *ibid.*, **21**, 294 (1917). Pyridine is used as solvent in preparing some metals, e.g., Li, by electrolysis.

[8] Bruner, *Z. Elektrochem.*, **16**, 204 (1910); *Bull. Acad. Sci. Cracov.*, 731 (1907).

[9] Bruner and Galecki, *Z. physik. Chem.*, **84**, 513 (1913).

[10] Röhler, *Z. Elektrochem.*, **16**, 419 (1910); Walden, *Bull. Acad. Sci. Petersb.*, **5**, 1055 (1911); Davis and Johnson, *Carnegie Inst. Pub.*, **260**, 71 (1918); Jones, Davis and Putnam, *J. Franklin Inst.*, **180**, 567 (1915); other organic solvents, Walden, *loc. cit.*, **7**, 559, 907 (1913).

[11] See Kraus, Electrically Conducting Systems, 1922.

[12] Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900).

[13] *Z. physik. Chem.*, **69**, 272 (1909); cf. Franklin and Gibbs, *J. Am. Chem. Soc.*, **29**, 1389 (1907) (methylamine).

Liquid halogens,[3] halogen hydracids,[4] glycerol,[5] benzene,[6] chloroform,[7] hydrogen peroxide,[8] sulphur dioxide,[9] aluminium bromide,[10] sulphuric acid,[11] hydrocyanic acid,[12] and other non-aqueous solvents have been examined. The classical researches are those of Walden,[13] who examined a large number of substances (PCl_3, $POCl_3$, PBr_3, $AsBr_3$, SO_2, SO_3, $SOCl_2$, SO_2Cl_2, S_2Cl_2, H_2SO_4, $SbCl_3$, $SbCl_5$, BCl_3, $SiCl_4$, $SnCl_4$, Br_2, $SO_2(OH)Cl$, $SO_2(OCH_3)_2$, organic solvents) and gives extensive references to the literature.

Svedberg[14] finds that the temperature coefficient of conductivity in anisotropic solvents is abnormally high; a sharp change in conductivity occurs at the transition point.

Temperature Coefficient of Conductivity in Non-Aqueous Solutions: The conductivity of many salts in organic solvents increases with temperature.[15] At certain concentrations and above certain temperatures the conductivity decreases with rise of temperature, and at lower temperatures there is usually a maximum point.[16] At concentrations about normal, and above, the conductivity increases steadily with rise of temperature. At higher concentrations the temperature coefficients are often very high. The effects may be interpreted on the lines of increased fluidity with rise of temperature, giving rise to an increase on conductance, and decreasing ionization, giving rise to a decrease in conductance. In very dilute solutions where the ionization is great, the conductance increases with rise in temperature because of the increasing fluidity. At certain intermediate concentrations and above certain temperatures, the conductance decreases, although at much lower temperatures the curve passes through a minimum. At high concentrations the temperature coefficient is again positive. The curves in Fig. 22[1] show the results obtained with KI in methylamine at different dilutions. The approximate equality between conductance and fluidity temperature coefficients found for aqueous solutions by Kohlrausch (see p. 539) was found also for non-aqueous solutions by Walden (*loc. cit.*). The results of Archibald[2] for the temperature

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[1] Kraus, *J. Am. Chem. Soc.*, **30**, 653, 1197, 1323 (1908), **36**, 864 (1914), **43**, 749 (1921).

[2] Kraus and Lucasse, *J. Am. Chem. Soc.*, **43**, 2529 (1921).

[3] Plotnikoff, *J. Russ. Phys. Chem. Soc.*, **49**, 76 (1917), Plotnikoff and Rokotjan, *ibid.*, **45**, 193 (1913); *C. A.*, **7**, 2148 (1913), Johnson and McIntosh. *J. Am. Chem. Soc.*, **31**, 1138 (1909); Mennie and McIntosh, *Trans. Roy. Soc. Canada*, **16**, iii, 301 (1922), Walden, see below.

[4] Archibald, *J. Am. Chem. Soc.*, **34**, 584 (1912), **29**, 665, 1416 (1907).

[5] Guy and Jones, *Am. Chem. J.*, **46**, 131 (1911).

[6] Allen, *Kansas Univ. Sci. Bull.*, 1905, Cady and Lichtenwalter, *J. Am. Chem. Soc.*, **35**, 1434 (1913); Koenig, *ibid.*, **36**, 951 (1914), Cady and Baldwin, *ibid.*, **43**, 646 (1921) (benzene solutions of dry salts have a real conductivity).

[7] Walden, *Bull. Acad. Sci. Petersb.*, **7**, 907 (1913), also CCl_4, *Z. anorg. Chem.*, **115**, 49 (1921) (summary of results for organic solvents).

[8] Jones and Murray, *Am. Chem. J.*, **30**, 205 (1903) (sulphuric and acetic acids more strongly ionized than in water).

[9] Walden; Dutoit and Gyr, *J. Chim. Phys.*, **7**, 189 (1909), Franklin, *J. Phys. Chem.*, **15**, 675 (1911).

[10] Izbekoff and Plotnikoff, *J. Russ. Phys. Chem. Soc.*, **43**, 18 (1911); *Z. anorg. Chem.*, **71**, 328 (1911).

[11] Kendall, Adler and Davidson, *J. Am. Chem. Soc.*, **43**, 1846 (1921).

[12] Kahlenberg and Schlundt, *J. Phys. Chem.*, **6**, 447 (1902).

[13] *Ber.*, **32**, 2862 (1900); *Z. anorg. Chem.*, **25**, 209 (1900); **29**, 371 (1902); Elektrochemie nichtwässriger Lösungen, 1924.

[14] *Ann. Physik*, **49**, 437 (1916); *Koll. Z.*, **18**, 101 (1916); **20**, 73 (1917), **21**, 19 (1917).

[15] Partington, *J. Chem. Soc.*, **99**, 1937 (1911), Rimbach and Weitzel, *Z. physik. Chem.*, **79**, 279 (1912); Walden and Centnerszwer, *ibid.*, **39**, 513 (1902); Walden, *ibid.*, **73**, 257 (1910); Kraus and Lucasse, *J. Am. Chem. Soc.*, **44**, 1941 (1922); Archibald, *J. Chim. Phys.*, **11**, 741 (1913); Elsey, *J. Am. Chem. Soc.*, **42**, 2454 (1920); Kraus, Electrically Conducting Systems, pp. 154 ff.; numerous papers by H. C. Jones and co-workers in *Am. Chem. J.* and *J. Am. Chem. Soc.* from 1903 onwards; Müller, *Ahrens Sammlung*, **27**, 279 (1923).

[16] Kraus, *loc. cit.*, p. 154.

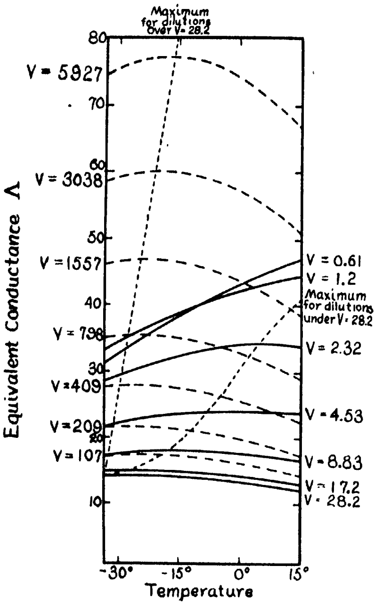

FIG. 22. Conductance-Temperature Curves for KI in Methylamine

TABLE XII

SOLUTIONS IN HBr. VALUES OF $\alpha \times 100$

	V_1	α_1	V_2	α_2
Acetic acid	4.30	2.62	0.571	2.72
Butyric acid	4.18	2.68	0.817	3.70
Benzoic acid	8.82	0.53	2.38	0.72
m-Cresol	15.0	− 7.71	1.00	+ 1.16
Thymol	43.6	0.47	7.34	0.00

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[1] Kraus, *loc. cit.*, Fig. 37, p. 164.

[2] *J. Chim. Phys.*, **11**, 741 (1913); cf. Fitzgerald, *J. Phys. Chem.*, **16**, 621 (1912); Franklin, *ibid.*, **15**, 675 (1911). In the immediate vicinity of the critical point the temperature-coefficient curves are discontinuous. Apparently the solvent vapors dissolve electrolyte. Kraus, *Phys. Rev.*, **18**, 40, 89 (1904); cf. Tyrer, *J. Chem. Soc.*, **97**, 621 (1910) (critical points of solutions, and solubilities above the critical point).

coefficient (α) in solutions in liquid HBr at different dilutions (V) show how varied are the numerical values for different electrolytes.

The results have been interpreted by Kraus on the basis of his equation for conductance as related to concentration (see p. 529). With rise of temperature the dielectric constant of the solvent decreases, and hence the mass action constant K also decreases. The value of m in the equation:

$$K' = H(c\alpha)^m + K$$

increases and H remains practically independent of the dielectric constant when the latter decreases.[1] The interpretation of the results, however, is obviously not confined to any special equation such as Kraus's.

The *effect of pressure* on the conductivity of non-aqueous solutions has been considered by Schmidt,[2] who divides it into three factors:

(i) change of volume; (ii) change of viscosity; (iii) change of ionization. The resistance at p atm. pressure is related to that at 1 atm. by the equation:

$$\log (r_p/r_1) = Ap - Bp^2,$$

where A, B are constants. At 20° C.,

$$A = 0.000106 + 0.00561\eta,$$

where η = viscosity for normal and slightly associated substances. In the case of strongly associated solvents (alcohols) the observed value of A is smaller; A also decreases with rise of temperature. The pressure coefficient is usually larger for aqueous solutions.

Viscosity and Conductivity: The same considerations apply to non-aqueous as to aqueous solutions with respect to the effect of viscosity on the motion of the ions. From the measurements of conductivities of solutions of tetraethylammonium iodide in various organic solvents Walden[3] was led to the generalization that the product of the molar conductance at infinite dilution and the viscosity of the solvent is constant, $\mu_\infty \eta_\infty$ = const. The constant is about 0.7, and is independent of temperature. At first Walden considered that the constant was independent of the solvent, but this was disproved by Pissarjewski and Shapovalenko.[4]

The empirical rule of Walden is not of general validity,[5] although it is an approximation which holds good in many cases. Walden[6] tested it for a large number of solutions. In the cases of $N(C_2H_5)_4I$ in benzyl cyanide, and $N(C_5H_{11})_4I$ in methyl and ethyl alcohols and acetone, the results showed that the salts of complex kations behaved exactly like KI. It was found that if V is the molar volume of a large ion, the relation $\Lambda_\infty\eta_\infty \sqrt[3]{V}$ = const. holds for different salts of a homologous series. Fitzgerald[1] applied Walden's relation to solutions in SO_2, NH_3 and methylamine. The constant fell between 0.9 and 1.1, and the conclusion was reached that these solvents are abnormal, but Walden[2] showed that for binary electrolytes the constant may vary from 0.5 to 1.0.

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[1] Electrically Conducting Systems, p. 155.

[2] *Z. physik. Chem.*, **75**, 305 (1910).

[3] *Z. physik. Chem.*, **55**, 207, 246 (1906); the relation follows from Stokes's law, Lungo, *Nuovo Cim.*, **16**, ii, 173 (1918).

[4] *J. Russ. Phys. Chem. Soc.*, **42**, 905 (1910); *C. A.*, **6**, 318 (1912); Walden, *Z. anorg. Chem.*, **113**, 85 (1920).

[5] Dutoit and Duperthuis, *J. Chim. Phys.*, **6**, 726 (1908); criticized by Walden, *Z. physik. Chem.*, **78**, 257 (1912).

[6] *Bull. Acad. Sci. Petersb.*, **7**, 559 (1913).

Arndt[3] found that Walden's rule, $\Lambda\eta$ = const., does not hold even approximately for fused $NaPO_3$ and mixtures of this with B_2O_3, below 900°. Above this temperature the relation applies.

Walden has recently shown, from a consideration of a large amount of experimental data,[4] that his rule holds for many acids and some salts in non-aqueous solvents, mixtures of solvents, and for aqueous solutions of salts yielding highly complex ions. The temperature coefficients of viscosity and of limiting conductance are practically identical:

$$1/\Lambda_\infty . d\Lambda_\infty/dt = -1/\eta_\infty . d\eta_\infty/dt,$$

as required by the rule. It does not hold for solvents which are highly associated, or which have a high viscosity, such as glycerol, formamide, etc.,[5] probably because temperature and concentration changes affect the degree of solvation of the solute. Robertson and Acree[6] find the relation

$$\alpha = \mu_v\eta_v/\mu_\infty\eta_\infty$$

to be less accurate for alcoholic solutions of concentration below $N/4$ than the simple Arrhenius formula: $\alpha = \mu_v/\mu_\infty$. This type of viscosity correction, in fact, is by no means so certain as seems to be assumed.

H. C. Jones[7] proposed the relation $\Lambda\eta/x$ = const., where Λ is the equivalent conductance of comparable equivalent solutions and x the association factor of the solvent. This was shown by Creighton[8] to hold approximately for solutions of *p*-tolyltrimethylammonium iodide in organic solvents. The expression $\Lambda_\infty\eta$ = const., also due to Jones, held for many of the solutions.

Sachanov and Prsheborovski,[9] as a result of experiments with solutions of silver nitrate in amylamine, aniline, quinoline, and other solvents, conclude that the maximum conductance shown by these solutions is a consequence of the overcompensation of the increase in dissociation of the solute by the excessive increase in viscosity of the solutions with concentration. The ab- with low dielectric constants (less than 13) the viscosity increases very rapidly with concentration. With solvents of high dielectric constant the molar conductance diminishes uninterruptedly with concentration, whilst if a viscosity correction is applied a minimum conductance is found.[1]

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[1] *J. Phys. Chem.*, **16**, 621 (1912).

[2] *Z. anorg. Chem.*, **113**, 85 (1920).

[3] *Z. Elektrochem.*, **13**, 809 (1907).

[4] *Z. anorg. Chem.*, **113**, 85 (1920).

[5] Pissarjewsky and Shapovalenko, *J. Russ. Phys. Chem. Soc.*, **42**, 905 (1910); *C. A.*, **6**, 318 (1912).

[6] *J. Phys. Chem.*, **19**, 381 (1915).

[7] *Am. Chem. J.*, **32**, 521 (1904); Jones and Bingham, *ibid.*, **34**, 481 (1905), pointed out that no allowance was made for possible changes in size of the ionic sphere.

[8] *J. Franklin Inst.*, **187**, 313 (1919).

[9] *J. Russ. Phys. Chem. Soc.*, **47**, 849 (1915); *C. A.*, **9**, 3009 (1915).

Dielectric Constant and Conductance: The force exerted between two charged point sources depends not only on the charges, q_1, q_2, and the distance d apart, but also, as was shown by Faraday,[2] on the nature of the medium separating them:

$$F = q_1q_2/Dd^2,$$

where D is a constant for any particular medium, known as the dielectric constant (called the specific inductive capacity by Faraday). Its value depends on temperature. The following values[3] refer to 18° C.

TABLE XIII

DIELECTRIC CONSTANTS OF LIQUIDS

Liquid Hydrocyanic acid	96	Methylamine	10
Water	81	Phenol	9.7
Nitrobenzene	36	Acetic acid	9.7
Methyl alcohol	33	Aniline	7 28 7.5
Ethyl alcohol	26.1	Propionic acid	5 5
Ammonia	22	Chloroform	5
Sulphur dioxide	16.5	Ether	4
Pyridine	12 4	Carbon disulphide	2.6
Ethylene chloride	10	Benzene	2.3

A comparison of these numbers with the ionizing powers of the solvents reveals a close similarity, which seems first to have been pointed out by J. J. Thomson[4] and Nernst,[5] and is known as the Nernst-Thomson rule: the ionizing power of a solvent is greater the larger the dielectric constant. The equation shows that the force between the pair of ions forming the salt "molecule" is smaller the larger the dielectric constant of the medium in which they are immersed, and they then fall apart more easily The Nernst-Thomson rule has been broadly confirmed by experiment.[6] There are other influences promoting ionization, and these appear most markedly when the dielectric constant is small; the chemical character of the solvent is then most important.[1] The dielectric constants of halogen hydrides (HBr, HI) are abnormally low, yet these solvents give solutions of high conductance with certain organic acids and alcohols.[2]

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[1] *J. Russ. Phys. Chem. Soc.*, **47**, 859 (1915), *C. A.*, **9**, 3009 (1915).

[2] Experimental Researches in Electricity, 11th Series, pp. 364, 393.

[3] Numerous other liquids, Schlundt, *J. Phys. Chem.*, **5**, 157, 503 (1901), Winkelmann's Physik, Vol. IV, 1905, pp. 135 ff.; also Graetz, Elektrizität und Magnetismus, Vol. I, 1918, pp. 157 ff.; Müller, *Ahrens Sammlung*, **27**, 213, 285 (1923).

[4] *Phil. Mag.*, **36**, 320 (1893).

[5] *Z. physik. Chem.*, **13**, 531 (1894).

[6] Schlundt and Palmer *J. Phys. Chem.*, **15**, 381 (1911); Sachanov and Prsheborovski, *Z. Elektrochem.*, **20**, 39 (1914); Joachim, *Ann. Physik*, **60**, 570 (1919).

The methods used in the determination of dielectric constants are:

(1) Condenser method, in which the capacity of a condenser is measured first with air as the dielectric and then with the liquid.[3] The dielectric constant of air may be taken as unity.

(2) Stationary wave method, in which[4] the lengths of stationary electromagnetic waves set up in the medium and in air are measured, the length being inversely proportional to $\sqrt{D}$.

The dielectric constants of many solvents have been measured by Walden,[5] who has also calculated the value for dissolved salts.[6] Formulæ have been proposed for the dielectric constants of solutions, e.g., by Silberstein:[7]

$$D = (V_1D_1 + V_2D_2)/(V_1 + V_2),$$

the mixture rule, and by Bouty:[8]

$$D = (M_1D_1 + M_2D_2)/(M_1 + M_2),$$

with masses instead of volumes.

The molar conductance of many solutions in solvents of small dielectric constant decreases with dilution. Solvents of high dielectric constant often show a negative viscosity effect, i.e., the viscosity of solutions decreases with increasing concentration.[9]

Dobrosserdoff[10] has found that Obach's relation:[11] $L = aD$, where L

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[1] Sachanoff, *J. Russ. Phys. Chem. Soc.*, **42**, 1363 (1910); *C. A.*, **6**, 179 (1912); **43**, 526 (1911); *C. A.*, **6**, 179 (1912); *Z. physik. Chem.*, **80**, 13, 20 (1912); cf. Plotnikoff and Rokotjan, *ibid.*, **45**, 193 (1913); *C. A.*, **7**, 2148 (1913); *ibid.*, **47**, 723 (1915); *C. A.*, **8**, 2475 (1914).

[2] Schaefer and Schlundt, *J. Phys. Chem.*, **13**, 669 (1909).

[3] Nernst, *Z. physik. Chem.*, **14**, 622 (1894); Turner, *ibid.*, **35**, 385 (1900); Tangl, *Ann. Physik*, **23**, 559 (1907); Joachim, *ibid.*, **60**, 570 (1919); for descriptions of all methods see Nernst, Theoretische Chemie, 8–10 Aufl., p. 367; Kohlrausch, Praktische Physik, 11 Aufl., pp. 616 ff.; Arndt, Physikal-Chem. Technik, 1915, pp. 611 ff.; Graetz, *loc. cit.;* Winkelmann, *loc. cit.* Other methods: Hertwig, *Ann. Physik*, **42**, 1099 (1913); Jackson, *Phil. Mag.*, **43**, 481 (1922); King and Patrick, *J. Am. Chem. Soc.*, **43**, 1835 (1921); Silow's electrometer method, Cohn and Arons, *Ann. Physik*, **33**, 13 (1888). The two methods mentioned in the text have been used with success by the writer.

[4] Drude, *Z. physik. Chem.*, **23**, 267 (1897); **40**, 635 (1902).

[5] *Z. physik. Chem.*, **70**, 569 (1910); Schaefer and Schlundt, *J. Phys. Chem.*, **13**, 669 (1909); **16**, 253 (1912); Schlundt and Underwood, *ibid.*, **19**, 338 (1915); Cauwood and Turner, *J. Chem. Soc.*, **107**, 276 (1915); Ratz, *Z. physik. Chem.*, **19**, 94 (1896); Schlundt, *loc. cit.*

[6] *Bull. Acad. Sci. Petersb.*, **6**, 305, 1055 (1912).

[7] *Ann. Physik*, **56**, 661 (1895).

[8] *Compt. rend.*, **114**, 1421 (1892); Philip, *Z. physik. Chem.*, **24**, 18 (1897). Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, **44**, 396, 679 (1912); *C. A.*, **6**, 1564, 2350 (1912), finds that the formulæ are not satisfactory; cf. Fürth, *Ann. Physik*, **70**, 63 (1923), who found, for instance, that the constant for a crystalline solute cannot be found from the mixture rule.

[9] Sachanov and Prsheborovski, *Z. Elektrochem.*, **20**, 39 (1914); Kraus and Bray, *J. Am. Chem. Soc.*, **35**, 1315 (1913).

[10] *J. Russ. Phys. Chem. Soc.*, **41**, 1385 (1909); *C. A.*, **5**, 607 (1911).

[11] Cf. Grimm and Patrick, *J. Am. Chem. Soc.*, **45**, 2794 (1923).

= latent heat of evaporation and a is a constant in a given homologous series (39.5 for aliphatic acids; 25.5 for amines; 31 for aromatic hydrocarbons; 14.2 for all esters; 6.5 for alcohols, nitriles,[1] ketones and alkyl halides), is of fairly wide applicability. Thwing's relation:

$$D = d(a_1k_1 + a_2k_2 + \cdots)/M,$$

where d = density, M = molar weight, a_1, a_2, $\cdots$ = number of atoms, k_1, k_2, $\cdots$ = dielectric constants of separate atoms, does not hold generally. Lang's relation:

$$D = 121.10^{-6}S + 1,$$

where S = sum of valencies of atoms, holds only for six gases. The same author has reached the following general conclusions as to the dielectric constant:[2] (1) It is a constitutive property. (2) In homologous series it decreases with increasing molecular weight.[4] (3) Large differences in D are produced by multivalent elements, e.g., nitrogen. (4) The effect on D produced by the entry of any one radical into a compound varies with the compound. (5) Change from a saturated to an unsaturated compound is accompanied by increase in D. (6) D increases with the symmetry of the compound, e.g., ring closure increases D. (7) Isomeric compounds have different D's.

Rise in temperature diminishes D in the case of liquids and gases, but increases it in the case of solids. According to Thomson[3] the change in D for liquids and gases is inversely proportional to the absolute temperature. The dielectric constants at the critical temperature are very small.[4]

Fleming and Dewar[5] measured the dielectric constants of several liquids at low temperatures; the constant for the solidified substance appears to decrease as the temperature falls.

The effect of pressure for liquids is given by the empirical formula:[6]

$$D_p = D_1(1 + Ap + Bp^2),$$

in which A is positive and B negative.

	MeOH	EtOH	Me_2CO	Et_2O	CS_2	$C_6H_5NH_2$
D at 15° C.	34.0	25.8	21.85	4.25	2.67	7.51
D at − 185° C.	3.13	3.11	2.12	2.31	2.24	2.92

The figures for ice are:

t° C.	− 206	− 182	− 175	− 149	− 136	− 111	− 77.7	− 49.0	− 7.5
D_t	2.43	2.42	2.43	3.43	5.02	10.8	37.3	57.2	70.8

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[1] Cf. Schlundt, *J. Phys. Chem.*, **5**, 503 (1901).

[2] *J. Russ. Phys. Chem. Soc.*, **43**, 73 (1911); cf. *C. A.*, **5**, 3362 (1911).

[3] *Phil. Mag.*, **27**, 764 (1914).

[4] Eversheim, *Ann. Physik*, **8**, 539 (1902); **13**, 492 (1904).

[5] *Proc. Roy. Soc.*, **61**, 299, 316, 358, 368 (1897).

[6] Ortway, *Ann. Physik*, **36**, 1 (1911); ether, benzene, toluene, xylene, CS_2, castor oil, etc.

Walden[2] has put forward the rule:

$$(1 - \alpha) = \text{const. } c^{1/3}/D, \text{ approximately,}$$

where c is the concentration, or $Dv^{1/3}$ = const. at a given temperature, for different solvents, where v is the dilution at which the solutions of a given electrolyte have the same ionization. This is in agreement with Ghosh's theory (see p. 564), but the values of the "constant" vary by as much as 23 per cent,[1] and Walden's rule cannot hold generally.

If K is the constant of the Ostwald dilution law at infinite dilution $K = (0.0054D)^3$, or generally, K = const. D^3. It follows that similar formulæ hold for polymerizing solvents.[2]

The influence of small quantities of salts on the dielectric constants of solvents has been studied by many experimenters, with most divergent results.[3] Walden considers that dissolved salts cause a large increase in the value of D, and is inclined to explain the abnormalities of strong electrolytes by the increase in the ionizing power of the solvent. Lattey found exactly the opposite result, D being lowered.

Maxwell[4] deduced the relation $n = D^{1/2}$, where n = refractive index, from the electromagnetic theory of light. This is in agreement with experiment in some cases, but the divergencies are enormous in the case of water and alcohol. The divergencies are attributed to the difference in the frequencies in the light waves and those used in finding the values of D. For very long waves, n has the required value for water.

Clausius and Mosotti[5] deduced the relation:

$$(D - 1)/(D + 2)d = \text{const.},$$

where d is the density. Walden[6] finds that the constant varies with temperature, sometimes increasing and sometimes decreasing with rise of temperature. He proposes the empirical relations:

$$\frac{D - 1}{D + 2} \cdot \frac{M}{d} \frac{\sigma}{T_s} = \text{const.} = 3.6,$$

where T_s is the absolute boiling point, and σ is the surface tension, and

$$MD = 0.18T_s.$$

These do not hold for associated liquids.

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[1] Partington, *Trans. Farad. Soc.*, **15**, 113 (1919); Kraus, Electrically Conducting Systems, p. 97; Turner and Bissett, *J. Chem. Soc.*, **105**, 947 (1914).

[2] Walden, *Z. physik. Chem.*, **94**, 263, 295, 374 (1920); **54**, 129 (1906); **70**, 569 (1910).

[3] Cohn, *Ann. Physik*, **45**, 370 (1892); Nernst, *Z. physik. Chem.*, **14**, 622 (1894); Drude, *ibid.*, **23**, 267 (1897); Smale, *Ann. Physik*, **61**, 625 (1897); Palmer, *Phys. Rev.*, **14**, 38 (1902); Walden, *Bull. Acad. Sci. Petersb.*, **6**, 305, 1055 (1912); Lattey, *Phil. Mag.*, **41**, 829 (1921).

[4] Electricity and Magnetism, Oxford, 1892, Vol. II, pp. 434 ff.

[5] Mechanische Wärmetheorie (Clausius), 1876, Vol. 2, p. 94. Cf. Pagliani, *Acc. dei Lincei*, **2**, 48 (1893).

[6] *Z. physik. Chem.*, **70**, 569 (1910).

Solvents with considerable ionizing power have a strong tendency to associate in the liquid state;[1] this agrees with the observation of Kohlrausch that pure liquids do not conduct at ordinary temperature to any appreciable extent. The degree of association of a binary solute in a non-aqueous solvent depends on the dielectric constant, increasing with falling dielectric constant.[2] Walden concludes that highly associated binary electrolytes may pass through all stages of molecular complexity, from simple ions to highly complex molecules, in suitable solvents. Sodium chloride in benzene is colloidal.

The Nature of Non-Aqueous Solutions: After the successful application of Arrhenius' theory of electrolytic dissociation to aqueous solutions it seemed obvious that the results obtained with other solvents should be capable of interpretation in a similar way. With the progress of investigation, however, serious difficulties were encountered. In some cases the molar conductance diminishes with increasing dilution, instead of increasing to a limit as it should on the theory of ionization. In the early days of the ionic theory the assumption was made that all reactions are ionic, and the curious arrest of many reactions in carefully dried systems lent some support to this sweeping generalization. Careful experiments showed[3] that reactions can take place in non-aqueous solutions which show no trace of conductance. On the other hand, earlier experiments of this type,[4] brought up as evidence against the ionic theory, have been shown[5] to be incorrect; solutions of copper salts in dry benzene have a definite conductance.

Other experimenters[6] report that a limiting molar conductance is not reached at high dilution, whereas Robertson and Acree,[7] and Dhar and Bhattacharyya[8] obtained definite limiting conductances.

The question of the calculation of ionization from conductance has also received different answers. Kraus and Bray[9] consider that the ratio of molar to limiting conductance measures the ionization up to 1 *n*. when corrections for viscosity are applied. On the other hand, Snethlage[10] considers that solutions in ethyl and methyl alcohols may be divided into two groups: (1) strong electrolytes, such as HCl and salts, the properties of solutions of which are

[1] Nernst, *Z. physik. Chem.*, **14**, 622 (1894), Dutoit and Aston, *Compt. rend.*, **125**, 240 (1897); Kohlrausch, *Ann. Physik*, **159**, 270 (1875).

[2] Meldrum and Turner, *J. Chem. Soc.*, **93**, 876 (1908); **97**, 1605, 1805 (1910); Walden, *Kolloid Z.*, **27**, 97 (1920).

[3] Folin and Flanders, *J. Am. Chem. Soc*, **34**, 774 (1912).

[4] Kahlenberg, *J. Phys. Chem.*, **5**, 339 (1901), **6**, 1 (1902); cf. Hughes, *Phil. Mag.*, **35**, 533 (1893); Sammis, *J. Phys. Chem.*, **10**, 593 (1906); Gates, *ibid.*, **15**, 97 (1911).

[5] Cady and Lichtenwalter, *J. Am. Chem. Soc.*, **35**, 1434 (1913).

[6] Shaw, *J. Phys. Chem.*, **17**, 162 (1913); cf. Plotnikoff, *J. Russ. Phys. Chem. Soc.*, **42**, 1589 (1910).

[7] *Eighth Internat. Congress Appl. Chem.*, **26**, 609 (1912).

[8] *Z. anorg. Chem.*, **82**, 357 (1913), cf. Partington, *J. Chem. Soc.*, **99**, 1937 (1911) (HCl in ethyl alcohol has a limiting conductance when moisture is excluded).

[9] *J. Am. Chem. Soc.*, **35**, 1315 (1913); see the admirable discussion of the problem in Kraus, Electrically Conducting Systems, 1922.

[10] *Z. physik. Chem.*, **90**, 1 (1915); Snethlage's hypothesis has been subjected to severe criticism by Dhar, *Trans. Farad. Soc.*, **15**, 81 (1919).

functions of the total concentration of electrolyte; (2) most organic bases and acids, which do not show this proportionality. For the first class, the ionization, it is stated, cannot be measured by the ratio of the conductances, but this ratio expresses the ratio of active to inactive molecules. The "activation" of a molecule is explained by the introduction of an electron into it, rendering it bipolar, but no division into free ions takes place. Snethlage's view does not seem to afford much assistance in the study of solutions. It may also be noted that the interpretation of ionization phenomena from results in chemical kinetics (velocity of reaction) is a matter of great delicacy, and that conclusions drawn in this field must be accepted with some caution.

Walden [1] found that the value of $\alpha = \Lambda/\Lambda_\infty$ (Λ_∞ obtained by extrapolation) is the same (0.666) for *saturated* solutions of NMe_4I, NEt_4I, and NPr_4I in different solvents.

The question of the applicability of the law of mass action to non-aqueous solutions has been fairly exhaustively studied.[2] In some cases the Ostwald dilution law is followed. Thus, solutions of ammonium formate in anhydrous formic acid obey the law in concentrated solutions;[3] fairly concentrated solutions of rosaniline hydrochloride in ethyl and methyl alcohols follow the law,[4] although aqueous solutions do not. In other cases the Rudolphi dilution law (p. 560) can be applied.[5] The equation of Kraus and Bray (see p. 529) has been applied to non-aqueous solutions with some success. In many solutions in ammonia the law of mass action holds good, and the smaller the ionization of an electrolyte the higher is the total concentration up to which the law of mass action applies.[6] This, it may be noted, is in agreement with the theory proposed by the writer [7] that the deviations from the law of mass action are due to free ions. Kraus and Bray found that the limiting concentration of the ions of strong electrolytes up to which the mass law held was approximately the same for solutions of a given electrolyte in different solvents, and for different electrolytes (strong and weak) in the same solvent. This again points to the ions as the disturbing cause.

The effect of the dielectric constant on the constants of the Kraus and Bray equation appears to be fairly regular. The equation has been tested in a number of cases,[8] and found to be satisfactory. The existence of a

[1] *Bull. Acad. Sci. Petersb.*, 7, 427 (1913).

[2] See the summary by Kraus, Electrically Conducting Systems, also Walden, Nichtwässriger Lösungen, 1924.

[3] Schlesinger and Calvert, *J. Am. Chem. Soc.*, 33, 1924 (1911).

[4] H. S. Davis, *Trans. Nova Scotia Inst. Sci.*, 13, 40 (1912); cf. Robertson and Acree, *J. Phys. Chem.*, 19, 381 (1915); Neale, *Trans. Farad. Soc.*, 17, 505 (1922); Jones and Mahin, *Z. physik. Chem.*, 69, 389 (1909); Schlesinger and Reed, *J. Am. Chem. Soc.*, 41, 1921 (1919); Schlesinger and Martin, *ibid.*, 36, 1589 (1914).

[5] Roshdestwensky and Lewis, *J. Chem. Soc.*, 99, 2138 (1911).

[6] Kraus and Bray, *J. Am. Chem. Soc.*, 35, 1315 (1913).

[7] Partington, *J. Chem. Soc.*, 97, 1158 (1910).

[8] Keyes and Winninghoff, *J. Am. Chem. Soc.*, 38, 1178 (1916); Darby, *ibid.*, 40, 347 (1918); Kraus and Kurtz, *ibid.*, 44, 2463 (1922); Kraus, Electrically Conducting Systems, 1922, pp. 67 ff.

true dissociation constant, K, at high dilution for all electrolytes may therefore be inferred.

Walden[1] considers that the heat of ionization of a salt has the same value in different solvents, but this has been contradicted by Dutoit and Aston.[2] Different heats of ionisation would imply interaction with solvent.

Calculations of the diameters of ions in non-aqueous solvents have been made by Walden[3] on the basis of the Stokes-Einstein equation (p. 552). For most ions the radii lie between 2.0×10^{-8} cm. and 3.9×10^{-8} cm., although that of the $H^{\cdot}$ ion is much smaller, 1.1×10^{-8} cm.,[4] and that of the $Li^{\cdot}$ ion much larger, 4.70×10^{-8} cm. The ionic radii in non-aqueous solutions follow the same order as in aqueous solutions: $H^{\cdot} < K^{\cdot} < Ag^{\cdot} < Na^{\cdot} < Li^{\cdot}$ and $Br' < I' < Cl' < NO_3'$. The ionic and atomic radii are practically the same, except for $H^{\cdot}$ and $Li^{\cdot}$, in the case of aqueous solutions, but in non-aqueous solutions the ionic radii are about twice as great. With organic anions and kations the radii are about the same in water and other solvents, the mean value being about 4.4×10^{-8} cm.

Walden[5] has put forward a rule by means of which the ionization of a salt in any solvent may be calculated from the dielectric constant D and viscosity η of the latter. This is a combination of the Ostwald-Bredig rule, and the relation

$$\Lambda_\infty = \Lambda_v + b/v^{0.45}$$

put forward by Lorenz.[6] These were combined with the relation

$$K = d_v D \eta_\infty v^{0.45}$$

found by Walden, in which d_v is given by the Ostwald-Bredig rule: $\Lambda_\infty = \Lambda_v + d_v$. Thence:

$$(1 - \alpha)D.v^{0.45} = 51.4/\Lambda_\infty \eta_\infty$$

or, since $\Lambda_\infty \eta_\infty$ is constant for many solutions (p. 591), it follows that:

$$(1 - \alpha)D.v^{0.45} = \text{const.},$$

or, for the same solvent,

$$(1 - \alpha)v^{0.45} = \text{const.}$$

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[1] *Z. physik. Chem.*, **59**, 192 (1907).

[2] *J. Chim. Phys.*, **6**, 699 (1908); Walden, *Z. physik. Chem.*, **78**, 257 (1912), maintains his position.

[3] *Z. anorg. Chem.*, **113**, 125 (1920).

[4] This is in agreement with the theory of Lapworth, see Lapworth and Fitzgerald, *J. Chem. Soc.*, **93**, 2167 (1908); Lapworth and Partington, *J. Chem. Soc.*, **97**, 19 (1910).

[5] *Z. anorg. Chem.*, **115**, 49 (1921).

[6] *Z. anorg. Chem.*, **108**, 81, 191 (1919).

Thus, if the value of $\Lambda_\infty \eta_\infty$ is known for a salt in any one solvent, the value of α in any other solvent at a given dilution may be calculated.[1]

Solvation:[2] The solvation hypothesis of Kohlrausch (p. 553)[3] has been extended to non-aqueous solutions.[4] Snethlage[5] considers that a large value of Λ_∞ indicates large solvation. Jones, Davis and Putnam[6] found that salts hydrated in aqueous solutions show evidence of solvation in formamide. The temperature coefficient of conductance is abnormally large when solvation is present. The temperature coefficient of conductance of sodium salts in ethyl alcohol is equal to the temperature coefficient of fluidity[7] between 0° and 30°, in agreement with Kohlrausch's theory.

Serkoff[8] pointed out that a compound such as lithium nitrate, the Li ion of which shows strong solvation, should exhibit a maximum conductance in mixtures of acetone and an alcohol, whilst potassium iodide should show no maximum. The salts KI, NaI and LiI showed no maximum, whilst LiCl did.

An attempt to calculate solvation has been made by Walden,[9] who found that

$$\Lambda_\infty \eta_\infty / \sqrt{M} = \text{const.} = 11.15 \text{ (approx.)}$$

held for many binary salts, mainly iodides, in a number of non-aqueous solvents (M = molar weight). If these salts are regarded as normal, the degree of solvation of other salts can be calculated in a manner similar to that used by Ramsay for associated liquids, and with similar uncertainty. An equation deduced by Herzog[10] may be used for the same purpose:

$$\Lambda_\infty \eta_\infty v^{1/3} = \text{const.},$$

where v = molar volume of salt. It gives practically the same results as Walden's.

Transport Numbers in Non-Aqueous Solutions: The method of determining transport numbers is essentially the same for non-aqueous as for aqueous solutions. The resistance is usually greater, so that there is greater danger of heating and convection, and it has also been found[11] that the middle portion of the solution, which should remain unchanged in composition, is usually situated near one of the electrodes, e.g., in the case of pyridine and acetonitrile solutions of silver nitrate, near the anode.[1]

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[1] Relation between solvent power and ionizing power: Walden, *Z. Elektrochem.*, **27**, 34 (1921). Sachanov, *J. Russ. Phys. Chem. Soc.*, **47**, 849, 859 (1915), considers that the ionization of a salt tends to a definite limit as the concentration increases.

[2] Cf. Müller, *Ahrens Sammlung*, **27**, 292 (1923).

[3] *Proc. Roy. Soc.*, **71**, 338 (1903)

[4] Jones and Carroll, *Am. Chem. J.*, **32**, 521 (1904); Jones, *ibid.*, **41**, 19 (1909).

[5] *Z. physik. Chem.*, **90**, 1 (1915).

[6] *J. Franklin Inst.*, **180**, 567 (1915).

[7] Bhattacharyya and Dhar, *Proc. K. Akad. Wetensch. Amst.*, **18**, 373 (1915).

[8] *J. Russ. Phys. Chem. Soc.*, **42**, 1 (1910); *Chem. Soc. Abs.*, 1910, **98**, (ii), 177.

[9] *Z. Elektrochem.*, **26**, 65 (1920); cf. Creighton, *J. Franklin Inst.*, **189**, 641 (1920).

[10] *Z. Elektrochem.*, **16**, 1003 (1910).

[11] Cf. Schlundt, Getman and Gibbons (refs. below).

The following table gives the transport numbers of the *kation* in solutions of silver nitrate according to the measurements of Schlundt,[2] Mather[3] and Campetti.[4]

TABLE XIV

TRANSPORT NUMBERS OF KATION IN SILVER NITRATE SOLUTIONS

t	Solvent	*D*	Volume in liters per mol. $AgNO_3$							
			0.42	1	2	4	10	16	35	40
	Water . . .	81	0 532	.500	.483	.473	—	—	—	.475
18°	Acetonitrile	35.8	—	.383	—	.422	.448	—	.473	—
15°	Methyl alcohol	33	—	—	—	—	—	.533		
20°	Ethyl alcohol	26 1	—	—	—	—	.405	.490		—
22°	Pyridine	12.4	—	.326	342	—	.390	—	—	.410

Sachanov and Grinbaum[5] used aniline ($D = 6.85$) and mixtures of aniline and pyridine ($D = 8.0$ and 9.7) with silver nitrate The transport number of silver diminished with increasing concentration for $AgNO_3$ in pyridine, acetonitrile, and the mixtures of aniline and pyridine, and for a given concentration was smaller the smaller was *D*. In aniline, the transport number increased with dilution, which may be connected with the formation of complex anions, of the type $Ag(NO_3)_2'$, and also complex kations. Krumreich[6] determined the transport numbers of $AgNO_3$ (0.01 *n*.) in mixtures of alcohol and water, by the direct method. The value of the transport number of the kation increased with the alcohol content up to about 30 per cent alcohol, and then decreased (at 40° C. with water, 0.4820; with 99.8 per cent alcohol, 0.4100). No secondary effects were noted, whereas Carrara[7] states that these occur.

Krüger[8] concluded, on theoretical grounds, that the transport numbers of a given pair of ions should tend to the same value in all non-associated solvents.

[1] Methods of determination, see, e.g., Hittorf. *Ann. Physik*, **106**, 551 (1859); Campetti, *Nuovo Cim.*, **35**, 225 (1894); Mather, *Am Chem. J*, **26**, 473 (1901), Schlundt, *J. Phys. Chem.*, **6**, 159 (1902); Getman and Gibbons, *J Am. Chem. Soc*, **36**, 1640 (1914); Sachanov and Grinbaum, *J. Russ. Phys. Chem. Soc*, **47**, 1769 (1915); *C. A.*, **10**, 2822 (1916), Krumreich, *Z. Elektrochem.*, **22**, 446 (1916), Frycz and Tolloczko, *Festschrift Univ. Lemberg*, **1**, 1 (1912); *Chem. Soc. Abstr.*, ii, 380 (1913), Sachanov, *J Phys. Chem*, **21**, 169 (1917), Schlesinger and Bunting, *J. Am. Chem. Soc.*, **41**, 1934 (1919), Franklin and Cady, *ibid.*, **26**, 499 (1904); Campetti, *Jahrb. Elektrochem.*, **1**, 22 (1895), Lapworth and Partington, *J. Chem. Soc.*, **99**, 1417 (1911): See also Müller, *Ahrens Sammlung*, **27**, 280 (1923).

[2] *J. Phys. Chem.*, **6**, 159 (1902).

[3] *Loc. cit*

[4] *Loc. cit.*

[5] *J. Russ. Phys. Chem. Soc.*, **47**, 1769 (1915), *C. A.*, **10**, 2822 (1916).

[6] *Z. Elektrochem.*, **22**, 446 (1916).

[7] *Gazz.*, **33**, 241 (1903); for criticism of Carrara's results see Lapworth and Partington, *J. Chem. Soc.*, **99**. 1417 (1911).

[8] *Z. Elcktrochem.*, **22**, 445 (1916).

In associated solvents, and when solvation occurs, the values differ. He remarks that in dilute solutions the transport numbers of silver nitrate are practically independent of the nature of the solvent.[1] Krüger believes that the effect of the solvent may be covered, in the simple case, by its viscosity: $u\eta = c_1$ and $v\eta = c_2$, where u and v are the mobilities and c_1, c_2 are constants.

The assumption that ions with large transport numbers are those common to solute and solvent[2] is probably true only in exceptional cases.[3]

Lapworth and Partington[4] determined the transport number of the Cl′ ion in alcoholic hydrochloric acid solution by measuring the electrode potentials of mercury and silver, the formula on p. 554 being applied. The value 0.37 at 25° C. was found, compared with 0.16 for aqueous solutions at the same temperature. The experiments of Lapworth and Hardman[5] confirm this value. The transport numbers of most ions, but not H˙, have the same value in alcohol as in water.[6]

Conductance in Mixed Solvents: Many measurements of conductance have been made[7] in mixed solvents, but the results are not easy to interpret. Several measurements with mixtures of water and alcohol are available.[8] The conductance of such solutions is lower than that in pure alcohol, and in some cases the conductivity curve exhibits a minimum for a certain mixture which corresponds with the maximum viscosity.

In mixed solvents containing acetone[9] the relations are complex.

Goldschmidt (*loc. cit.*) found that addition of water to alcoholic hydrogen chloride, lithium chloride, sodium chloride, etc., depressed Λ_∞ rapidly at first, then more slowly as more water was added, until the water was present in 2 *n* concentration, when the conductance increased on further addition. All acids which are slightly ionized in alcohol are affected in this way on addition of water.

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[1] Sachanov, *J. Phys. Chem.*, 21, 169 (1917).

[2] Frycz and Tolloczko, *Festschrift Univ. Lemberg*, 1, 1 (1912); *Chem. Soc. Abstr.*, ii, 380 (1913).

[3] Walden, *Z. Elektrochem.*, 26, 72 (1920).

[4] *J. Chem. Soc.*, 99, 1417 (1911).

[5] *J. Chem. Soc.*, 99, 2242 (1911); 101, 2249 (1912).

[6] Cf. Newbery, *J. Chem. Soc.*, 107, 1520 (1915), where other references are given.

[7] See Jones and co-workers in *Am. Chem. J.* from 1900 onwards; *Carnegie Inst. Reports*, No. 80 (1907), No. 180 (1913), No. 230 (1915).

[8] Zelinski and Krapiwin, *Z. physik. Chem.*, 21, 35 (1896); Serkoff, *J. Russ. Phys. Chem. Soc.*, 40, 399 (1908); 41, 1 (1909); 4, 1921 (1910); Hägglund, *Arkiv. Kem. Min. Geol.*, 4, No. 11, 1 (1911); Goldschmidt and co-workers, *Z. physik. Chem.*, 89, 129 (1915); 91, 46 (1916); *Z. Elektrochem.*, 19, 226 (1913); 20, 473 (1914); 22, 11 (1916); Jones, Wightman, Davis and Holmes, *J. Chim. Phys.*, 12, 385 (1914); Kremann and Brassert, *Monatsh.*, 31, 195 (1910); Kreider and Jones, *Am. Chem. J.*, 45, 282 (1911); Dorochevski and Dvorshontschik, *J. Russ. Phys. Chem. Soc.*, 46, 1676 (1914); *C. A.*, 9, 2173 (1915), who tested dilution formulæ of Lenz, *Beibl.*, 7, 399 (1887), Arrhenius, *Z. physik. Chem.*, 9, 487 (1892), and Wakeman, *ibid.*, 11, 49 (1893), and found the equation $\Lambda = A - a/\sqrt[n]{v}$ to apply within narrow limits; Jones and Lindsay, *Am. Chem. J.*, 28, 329 (1902).

[9] Serkoff, *loc. cit.*; Fischler, *Z. Elektrochem.*, 19, 126 (1913); Jones and Mahin, *Am. Chem. J.*, 41, 433 (1909); *Z. physik. Chem.*, 69, 389 (1909); Davis, Hughes and Jones, *Z. physik. Chem.*, 85, 513 (1913). Solutions containing glycerol: Pissarjewski and Shapovalenko, *J. Russ. Phys. Chem. Soc.*, 42, 905 (1910); *C. A.*, 6, 318 (1912); Guy and Jones, *Am. Chem. J.*, 46, 131 (1911); Davis, Putnam and Jones, *Z. physik. Chem.*, 90, 481 (1915). Formamide and alcohol: Davis and Johnson, *Carnegie Inst. Pub.*, 260, 71 (1918). Pyridine and water: Ghosh, *J. Chem. Soc.*, 117, 1390 (1920).

The results of all investigators show that the effect of changing viscosity on mixing solvents is important in affecting the conductance, but no general conclusions can, apparently, be drawn. In acetone solutions, for example, no parallelism exists between conductance and viscosity curves,[1] whilst in solutions containing glycerol a marked parallelism was found.[2] In some cases, when the added non-electrolyte forms a stable complex with one of the ions, there is a decrease in viscosity.[3] When combination ceases, there may then be an increase in viscosity on further addition of non-electrolyte.[4]

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[1] Serkoff, *loc. cit.*

[2] Guy and Jones, *loc. cit.*

[3] Blanchard, *J. Am. Chem. Soc.*, 26, 1315 (1904).

[4] Kraus, Electrically Conducting Systems, 1922, p. 119, who concludes that the conductance change is more nearly proportional to the fluidity change the smaller the molecules of the added non-electrolyte.

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